



3RD. INTERNATIONAL CONFERENCE
SOLAR ENERGY STORAGE AND
APPLIED PHOTOCHEMISTRY,
Cairo, Egypt
8-14 January 1995

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BOOK OF ABSTRACTS

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Third International Conference on
SOLAR ENERGY STORAGE AND APPLIED
PHOTOCHEMISTRY

8-14 JANUARY 1995, CAIRO, EGYPT

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Third International Conference on
SOLAR ENERGY STORAGE AND APPLIED
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M. S. A. ABDEL MOTTALEB (EDITOR)

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FORWARD

Welcome to the 3rd International Conference on Solar Energy Storage and Applied Photochemistry, January 8-14, 1995, Cairo, Egypt.

It is well known that mastery of modern science and technology is the key factor in the progress of developed countries. Over the past few decades, Egypt has become more involved in the promotion of basic education and research in widely diversified areas of science, as a stepping stone to more advanced technology. A broad-based approach to science is essential for research and development. An enormous effort is being made to promote education, research and technology in all areas of science that based on national as well as international collaboration. The Egyptian Government has recognized the significant effort of Ain Shams University (A.S.U.) to contribute in achieving this goal, with a kind financial contribution (\$600,000.0) offered through the Ministry of International Cooperation, to establish a science and technology center for Photoenergy. This Photoenergy Center is located in a separate building, under construction, at the Faculty of Science, A.S.U. Campus. The center will be involved in teaching and research. The research and training will be focussed on photochemical processes and Solar Chemistry, their industrial applications and environmental implications. This conference is the first major function of the Photoenergy Center.

This volume contains the abstracts of the invited lectures and posters. Each abstract is reproduced as submitted by the author, and arranged alphabetically using the name of the presenter at the conference. We are grateful to all participants who submitted abstracts in response to our call for contributed papers. The wide range of photochemical topics covered in these abstracts indicates the growing interest and development of photochemistry in recent years.

The finances of the conference have been managed through a combination of registration fees and generous support from a number of national and international sources. We would like to acknowledge all donors for their financial support. Particular thanks are due to Professor Dr. A. M. Abdel-Hafez, the authorities of Ain Shams University and Faculty of Science as well as the Department of Chemistry and all those who through sincere advice and assistance have contributed to make this conference a reality.

We would like also to thank all of you for coming and taking an active role in ensuring the success of this conference. We sincerely hope that the meeting will stimulate further interest among the Egyptian scientists and will enhance the scientific and personal contacts among all participants. We look forward to a fruitful scientific conference that we hope will educate all of us as well as stimulate new and creative research and collaboration to be reported at future conferences.

Sabry Abdel-Mottaleb

**The organizers thank deeply the following organizations
for their generous financial and moral support**

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Ministry of Petroleum

Ministry of International Cooperation

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International Centre for Science and High Technology

[ICTP, Trieste, Italy]

International Science Foundation (ISF)

European Research Office (ERO), US Army

Naval Research Office in Europe, US Navy

**A session will be sponsored by European Research Office
of US Airforce**

ABSTRACTS

The Rapid Deterioration of Anthracene Laser Dyes in Chlorinated Organic Solvents.

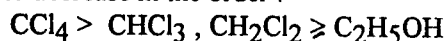
S. A. El- Daly, S. A. Azim, H. A. El- Daly, Kh. A. Abou- Zied
and E. M. Ebeid

(Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt), and

J. Heldt and J. R. Heldt

(Institute of Experimental Physics, University, PL - 80 - 952 Gdansk, Poland.)

The photochemical quantum yields (ϕ_c ; $\lambda_{ex} = 254$ nm) of five anthracene laser dyes (I- V) together with parent anthracene have been studied in different organic solvents e.g. CCl_4 , $CHCl_3$, CH_2Cl_2 and C_2H_5OH . The ϕ_c values are summarized in Table (1). The ϕ_c values in CCl_4 are several orders of magnitude higher than those in ethanol and the ϕ_c values decrease in the order :



The excited state lifetimes (τ) of these dyes in the some of these solvents have been measured in the presence and absence of molecular oxygen (Table 1). The data illustrates the role of molecular oxygen in fluorescence quenching. The second- order quenching rate constants of the quenching process have also been determined.

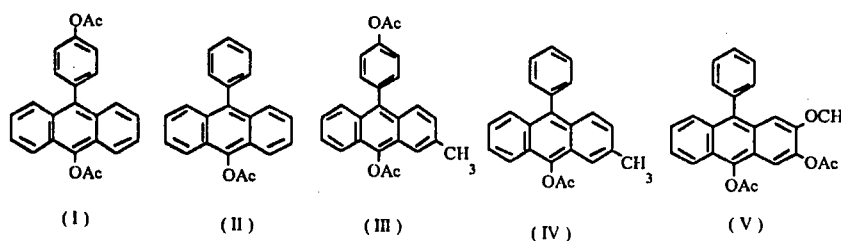


Table (1)

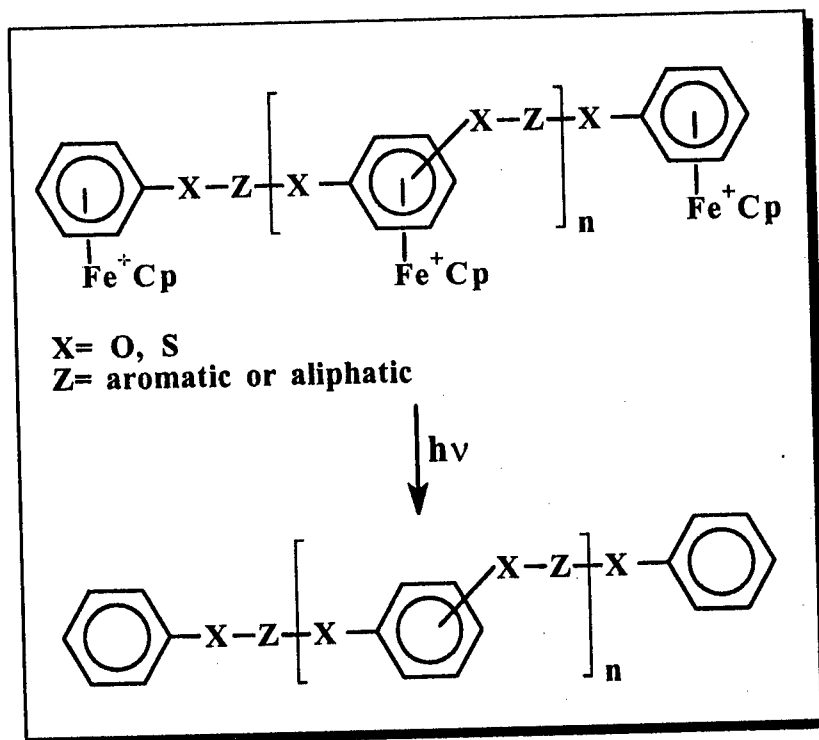
Compound	ϕ_c				Lifetime*			
					$CHCl_3$		C_2H_5OH	
	CCl_4	$CHCl_3$	CH_2Cl_2	C_2H_5OH	τ	τ_0	τ	τ_0
I	0.0701	0.0213	0.0071	0.0079	8.049	6.257	8.907	5.929
II	0.1672	0.0273	0.0088	0.0082	8.507	6.235	8.279	5.979
III	0.1584	0.0266	0.0090	0.0072	8.450	6.506	9.160	6.389
IV	0.1005	0.0296	0.0081	0.0068	8.802	6.759	9.450	6.357
V	0.0796	0.0196	0.0044	0.0038	10.157	7.430	11.33	7.420

* τ_0 and τ are the fluorescence lifetimes ($\lambda_{ex} = 365$ nm) in the presence and in the absence of O_2 .

PHOTOLYSIS OF POLYAROMATIC ETHERS AND THIOETHERS WITH PENDANT CYCLOPENTADIENYLIRON MOIETIES

Alaa S. Abd-El-Aziz*, Christine R. de Denus, and Karen M. Epp
Department of Chemistry, University of Winnipeg, Winnipeg,
Manitoba, Canada, R3B 2E9

Polyaromatic ethers and thioethers are undoubtedly important classes in the field of polymer chemistry due to their interesting electrical, mechanical, and thermal properties. Traditional routes to the synthesis of these systems suffer from various limitations such as harsh conditions, introducing certain functionalities, and low reaction yields. In the past few years we have developed a versatile and efficient route to the preparation of these compounds.¹ This involves the activation of a chloroarene with a cyclopentadienyliron moiety toward nucleophilic aromatic substitution leading to the formation of the title compounds. In this study we have used photolysis as a means to cleave these polyaromatic systems from their pendant cyclopentadienyliron moiety. Solutions of these complexes were subjected to intense visible light radiation for a period of 4 hours leading to the liberation of the free polyaromatic ethers and thioethers. Detailed experimental conditions and solvent studies will be presented.



1. (a) Abd-El-Aziz, A. S.; de Denus, C.R. *J. Chem. Soc. Chem. Commun.* 1994, 663.
- (b) Abd-El-Aziz, A.S.; Epp, K.M.; de Denus, C.R.; Fisher-Smith, G. *Organometallics*, 1994, 13, 2299.
- (c) Abd-El-Aziz, A. S.; Schriemer, D.C.; de Denus, C.R. *Organometallics*, 1994, 13, 374.

PHOTOCHEMICAL REACTION OF 4-NITROBENZYLIDENE MALONONITRILES WITH HYDROGEN DONORS

**F.M.ABD EL-LATIF*, M.A.BARSY, M.E.HASSAN, E.ABD EL-RADI and
M.A.EL-MAGHRABY**

**DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, ASSUIT
UNIVERSITY (ASWAN BRANCH), ASWAN, EGYPT**

Upon solar and/or ultraviolet irradiation, 4-nitrobenzylidene malononitrile derivatives reacted with triethylamine and/or isopropanol in benzene to give substitution and/or reduction products. Spectral analysis showed that one of the cyano group replaced by amine or isopropyl group. The hydroxylamine as well as the azo derivatives, as reduction product were isolated in the lower yield.

Homogeneous Photoinitiated Graft Copolymerization of 4-Vinyl Pyridine onto Ethyl Cellulose

E. M. Abdel-Bary, E. A. Abdel- Razik, A. A. Sarhan and N. M. Abdel-Salam
Chemistry Department, Faculty of Science, Mansoura University, Mansoura,
Egypt.

Homogeneous photoinduced graft copolymerization of 4-vinyl pyridine (4-VP) onto ethyl cellulose (EC) in the presence of different photosensitizers such as 1-acetonaphthone (1-AN), 2-acetonaphthone (2-AN) and biacetal (Bi) was carried out. The effects of different parameters such as type of photosensitizer, irradiation time, concentrations of monomer, substrate and initiator on the grafting parameters were investigated. The IR spectrum of EC-g-4-VP graft copolymer shows the appearance of new peaks between $1600\text{--}1690\text{ cm}^{-1}$ indicating the presence of poly-4-vinyl pyridine grafted chains. The rate of graft copolymerization of 4-vinyl pyridine onto EC in presence of 1-AN, 2-AN and Bi was found to be 0.098 %/min., 0.088%/min. and 0.042%/min. respectively. A good correlation was observed between the change of absorbance at λ_{max} 224 nm that belongs to pyridine rings in EC-g-4VP graft copolymer and the graft percentage value. A suitable mechanism for photoinduced grafting is suggested.

Charge Transfer Interactions and Efficiencies of Sensitized Singlet Oxygen Production from Substituted Biphenyls

A A Abdel-Shafi and F Wilkinson

Department of Chemistry, Loughborough University of Technology
Loughborough, Leicestershire, LE11 3TU, UK

Triplet states of biphenyl derivatives were produced by energy transfer with unit efficiency in the solvent acetonitrile. The bimolecular rate constants for oxygen quenching of these triplet states ($k_{O_2}^T$), the proportion of triplet states quenched by oxygen in air equilibrated solutions ($P_T^{O_2}$) and the fractional formation efficiencies of singlet oxygen produced for those triplet states which are quenched by oxygen (f_Δ^T), are reported for a range of biphenyl derivatives.

It has been observed that there is an inverse correlation between $k_{O_2}^T$ and f_Δ^T and a direct dependence of $k_{O_2}^T$ on the half-wave oxidation potentials of the biphenyl derivatives. These investigations establish the involvement of charge transfer interactions during oxygen quenching of these triplet states [cf. refs 1-3]. The reported values for $k_{O_2}^T$ extend from 1.26×10^{10} to $8.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ which cover a wide range of the theoretically expected values (max. $1.64 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ corresponding to 4/9 of the diffusion controlled rate). f_Δ^T values extend from 0.32 to 0.85.

References

1. D J McGarvey, P G Szekeres and F Wilkinson, *Chem. Phys. Lett.* 199 (1992) 314.
2. F Wilkinson, D J McGarvey and A F Olea, *J. Am. Chem. Soc.* 115 (1993) 12144.
3. F Wilkinson, D J McGarvey and A F Olea, *J. Phys. Chem.* 98 (1994) 3762.

Singlet-Singlet Energy Transfer Between Coumarin4-water Exciplex and Coumarin314 In Aqueous and Micellar Media

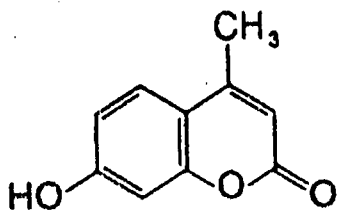
A.A.Abdel-Shafi and M.S.A.Abdel-Mottaleb

Photoenergy Centre, Faculty of Science, Ain Shams University,
Abbassia, Cairo, Egypt.

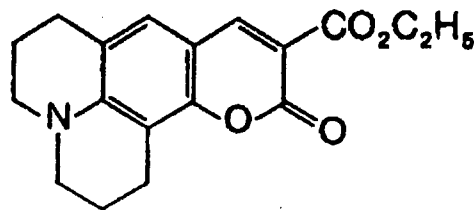
Singlet-singlet energy transfer from 7-hydroxy,4-methylcoumarin-water exciplex (as a donor) to coumarin314 (as an acceptor) is reported in aqueous and micellar solutions (in both cationic CTAB and anionic SDS surfactants).

The photophysics and excited state dynamics of the exciplex have been reported previously(1). In this contribution Stern-Volmer quenching constants, energy transfer distances, and energy transfer efficiencies in the different media are reported.

The preliminary investigations point to the involvement of long range dipole-dipole energy transfer pathway.



Coumarin 4



Coumarin 314

References

- 1) M.S.A.Abdel-Mottaleb, B.A.El-Sayed, M.M.Abo-Aly, and M.Y.El-Kady
J.Photochem.Photobiol., A:Chem., 46(1989)379.
- 2) S.E.Morsi and M.S.A.Abdel-Mottaleb, *Indian Academy of Sciences Proceedings*,
104(1992)81.
- 3) F.S.Abdel-Hamed, M.S.A.Abdel-Mottaleb, and A.A.Abdel-Shafi, *Spectrochimica Acta*,
in press.

ON THE PHOTOGENERATION OF PYRIDYLCARBENES

Aboel-Magd A. Abdel-Wahab, Mohamed T. Ismail, Omima S. Mohamed
Department of Chemistry, Faculty of Science, Assiut University
Assiut, Egypt.

and

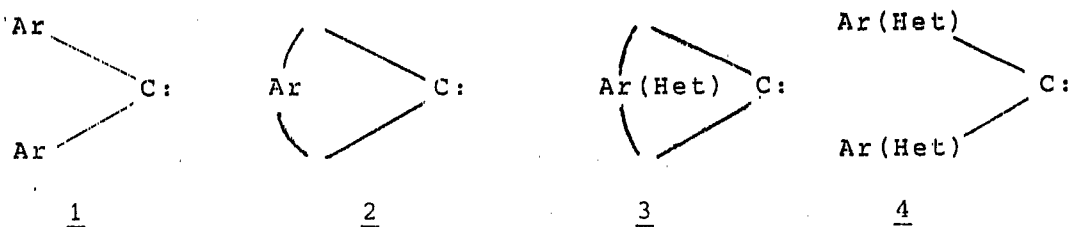
Heinz Durr

F.B.11.2, Org. Chemie, Universitat des Saarlandes, D-6600-Saarbrücken,
Germany.

The chemistry of diazafluorenylidene isomers varies distinctly from those of fluorenylidene or diarylcarbenes.

Continuation to these studies and related to the question of singlet-triplet equilibration of carbenes, attempts were directed in this work for the synthesis of noncondensed-heteroarylcarbenes.

Synthesis of pyridylcarbenes, for example, was attempted starting with the corresponding ketone via hydrazone formation, oxidation with metal oxides and photolysis of the oxidation product.



The products were separated and rigidly identified using elemental analysis, IR, ^1H NMR, ^{13}C NMR as well as MS.

References:

- 1- Y.Z.Li and G.B.Schuster
J.Org.Chem., 52, 3975 (1987).
- 2- O.S.Mohamed, H.Durr, M.T.Ismail and A.A.Abdel-Wahab
Tet.Lett., 30(15) 1935 (1989).
- 3- C.Mayor and C.Wentrup,
J.Am.Chem.Soc., 97, 7467 (1975).
- 4- A.A.Abdel-Wahab, M.T.Ismail, O.S.Mohamed and H.Durr
Chem.Ber.1994, submitted.

Environmental Degradation of Pesticides under the influence of light

Wafaa M. Abdou,* H. Wamhoff, M. R. Mahran and M. M. Sidky

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Institut für Organische Chemie und Biochemie der Universität Bonn, 5300 Bonn, FRG

Photodegradation of pesticides in the environment occurs in the atmosphere, in surface waters and on various solid surfaces such as soil and plants. An assessment of the importance of photodegradation on soil is difficult because it much depends on the nature of the compartment, the climatic conditions and the physicochemical properties of the compound under consideration.

As many investigations have revealed, visible and UV-light is responsible for the chemical alteration, rearrangements, destruction and decay of numerous organic compounds and also heterocyclic molecules.

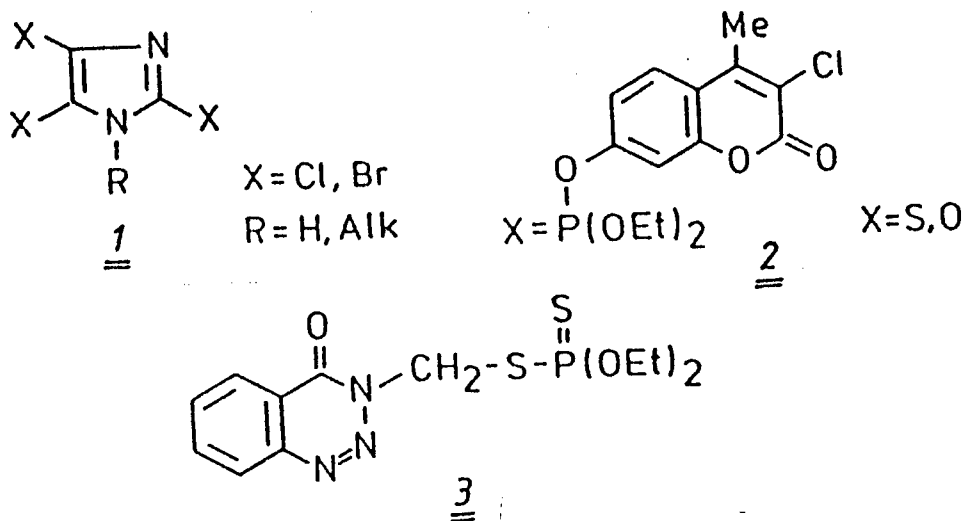
The present investigation deals with photodegradation studies on biological active, industrially produced and worldwide applied heterocyclic principles of the classes of herbicides, insecticides, pesticides as well as fungicides. In detail, the following model compounds have been irradiated in organic solvents.

Perhalogenimidazoles 1

Coumaphos, Coroxon, Potazan 2

Azinphos-Ethyl-(Gusathion) 3

In most cases, a rapid photodegradation, and as a consequence, a rapid decrease of the biological activities have been found. Effect of singlet oxygen on the degradation rate has also been studied. The photolysis schemes are discussed in details.



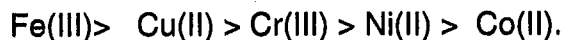
Analytical Determination of Iron (III): Fluorescence Quenching Technique

**M. M ABO-ALY, L. F. ISMAIEL, A. A. SHALABY, M. S. ANTONIOUS
AND M. S. A. ABDEL-MOTTALEB***

**DEPARTMENT OF CHEMISTRY AND PHOTOENERGY CENTRE*, FACULTY OF
SCIENCE, AIN SHAMS UNIVERSITY
ABBASSIA, CAIRO, EGYPT**

In continuation to our studies on the quenching of dye lasers by inorganic species using spectrofluorometric technique [1], we report here on the fluorescence quenching of fluorene and its aza derivative by some transition metal ions in ethanol.

Stern-Volmer rate constants and the activation energies were calculated for the quenching process. The results obtained clearly indicate that the electron transfer mechanism is the major deactivation pathway and the Ksv value decreases in the order:



The data obtained show that these fluorescent probes are of potential value in the analytical determination of trace amounts of iron (III) in presence of the other cations .

Synthesis of some Potential Photo-therapeutic and Singlet Oxygen Sensitizers : Hematoporphyrin - Coumarins (HPD-C) and Hematoporphyrin - Furocoumarins (HPD-FC).

M. M. Abou-Elzahab, M. El-Far, M. Abdel-Mogib and M. Eltantawy

Department of Chemistry and Biochemistry, Faculty of Science,
Mansoura University, Mansoura, A. R. Egypt.

Hematoporphyrin derivative (HPD) was reacted with 1,2-dichloroethane, the product was treated with coumarins or some natural furocoumarins to give new series of hematoporphyrin - coumarins (HPD-C) and hematoporphyrin - furocoumarins (HPD-FC) as new singlet oxygen and potential photo-therapeutic sensitizers.

The previouir photooxygenation studies of imperatorin using tetraphenylporphyrin (TPP) as singlet oxygen sensitizer gave two imperatorin - hydroperoxide derivatives¹.

The above reaction was repeated using the new series of HPD-C or HPD-FC derivatives instead of TPP to give the same previous products in different yields.

Reference :

- 1- M. M. Abou-Elzahab, W. Adam and C. R. Saha-Müller, Liebigs A Ann. Chem., 967 (1991).

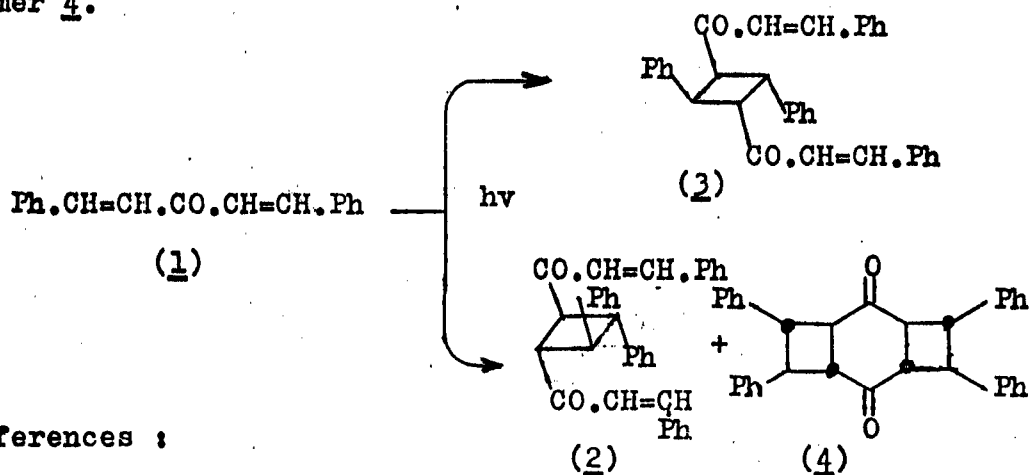
Photochemical Reactions of Dibenzalacetone

E. Elgendy, M. Hammouda, M. M. Abou-Elzahab and M. A. Metally

Department of Chemistry and Biochemistry, Faculty of Science,
Mansoura University, Mansoura, A. R. Egypt.

The photoirradiation of dibenzalacetone (1) in benzene and isopropanol gave head-to-head dimer (2)¹. Whereas, the irradiation in the solid state afforded head-to-tail syn dimer (3)².

In view of the previously reported cases, it seems of interest to study the behaviour of solvents towards the photoirradiation of 1 in benzene, 1,4-dioxane, methanol or ethanol for fourty hours gave head-to-head anti dimer (2), whereas, in acetic acid, the irradiation of 1 afforded the dimer 2 and the dimer 4.



References :

- 1- G. W. Recktenwald, J. N. Pitts and R. L. Letsinger, J. Am. Chem. Soc., 75, 3028 (1953).
- 2- M. Kofitory, K. Tanaka and F. Toda, J. Org. Chem., 50, 2154 (1985).

THE ROLE OF INORGANIC COMPLEXES IN ENERGY CONVERSION

L.F.M. Ismail, M.M. El-Fass, S.A.M. Abo-Farha
and M.S.A. Abdel-Mottaleb*

Department of Chemistry, Faculty of Science,
Al-Azhar University, Nasr City, Cairo, Egypt.

Photoenergy Centre, Faculty of Science, Ain-Shams
University, Abbassia, Cairo, Egypt.

Fluorescence quenching of the laser dyes coumarin 314 and 337 was studied by iron (III) 1, 10-phenanthroline (phen) and 2, 2'-bipyridyl (bipy) complexes in homogeneous aqueous solutions as well as in heterogenous solutions of cationic surfactant cetyl trimethylammonium bromide (CTAB⁺) and anionic surfactant sodium dodecyl sulphate (SDS⁻) at different temperatures. The Stern-Volmer constant (K_{sv}), the critical concentration (C_o), the critical radius (R_o) values and thermodynamic parameters ΔG , ΔH and ΔS were evaluated. The calculated K_{sv} values in CTAB⁺ are smaller than in water. This lowering in the quenching efficiency is due to the repulsive coulombic interactions between high positively charged quencher $[Fe(phen)]^{3+}$ or $[Fe(bipy)]^{3+}$ in the vicinity of the positively charged micelle. whereas, K_{sv} values in SDS⁻ are larger than in water. The obtained results suggest that the long-range energy transfer quenching mechanism is operative with R^o value $> 100 \text{ \AA}$.

Energy Transfer from 2, 5-Distyryl Pyrazine (DSP) and 2, 5- Bis 2(2-Naphthyl) Vinyl Pyrazine (B2NVP) to R6G.

S.A. El- Daly, S. A. Azim, H. A. El- Daly and Kh. A. Abou-Zied.

Department of Chemistry, Faculty of Science, Tanta Univ. Tanta, Egypt.

Energy transfer between the titled compounds has been studied using steady- state emission studies in two solvents of different viscosities namely isopropanol and ethylene glycol. The critical transfer distances (R_0) together with second order quenching rate constants based on corrected emission spectra have been measured. The values are summarized in table (1). The underlying mechanism of energy transfer is that of Förster type.

Table (1)

System	Isopropanol		Ethylene glycol	
	R_0 (Å)	k_q dm ³ mol ⁻¹ s ⁻¹	R_0 (Å)	k_q dm ³ mol ⁻¹ s ⁻¹
DSP/R6G	125.4	1.61×10^{13}	137.4	1.28×10^{14}
B2NVP/R6G	183.0	2.72×10^{13}	178.8	8.53×10^{13}

**STRUCTURES AND LASER INDUCED S_2 - S_0 FLUORESCENCE SPECTRA OF
VAN DER WAALS COMPLEXES OF AZULENE AND RELATED COMPOUNDS
IN A SUPERSONIC JET**

Osama K. Abou-Zied, Hemant K. Sinha, and Ronald P. Steer

**Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan,
Canada S7N 0W0**

The van der Waals complexes of azulene (AZ), 2-methylazulene (2-MAZ) and 1,3-dimethylazulene (1,3-DMAZ) with the rare gases and the C_1 to C_{10} normal alkanes and perfluoro-n-alkanes have been synthesized in a supersonic jet and investigated by laser-induced S_2 - S_0 fluorescence spectroscopy. The spectra of the rare gas complexes are consistent with shifts of the equilibrium positions of the adatoms along the long axes of the substrates on excitation, i.e. in the direction of the S_2 - S_0 transition moment. The structures, binding energies and vibrational frequencies of the ground state species have been calculated using the pairwise summation of atom-atom Lennard-Jones 6-12 potentials. The microscopic solvent shifts, $\Delta\bar{\nu}$, of the series of 1:1 complexes with normal alkanes are larger than those of the corresponding perfluoro-n-alkanes, despite the larger molecular polarizability of the latter. The values of $\Delta\bar{\nu}$ increase monotonically with carbon number of the adduct to C_5 in 1:1 n-alkane complexes with AZ and 1,3-DMAZ and to C_7 in 1:1 complexes with 2-MAZ. However, $\Delta\bar{\nu}$ exhibits no further significant change beyond C_3 in 1:1 perfluoro-n-alkane complexes. The results are interpreted in terms of a model in which the n-alkanes stretch out along the long axis of the chromophore and "wet" its surface whereas the perfluoro-n-alkanes bend away from the surface of the chromophore and tend to be "non-wetting".

CHARGE RECOMBINATION KINETICS OF PHOTOSYNTHETIC REACTION CENTERS IN PHOSPHOLIPID ORGANIZED SYSTEMS.

A. Agostiano*, L. Catucci*, M. Della Monica*, A. Mallardi*,
G. Palazzo* and G. Venturoli[§]

* Dipartimento di Chimica, Università di Bari, Italy

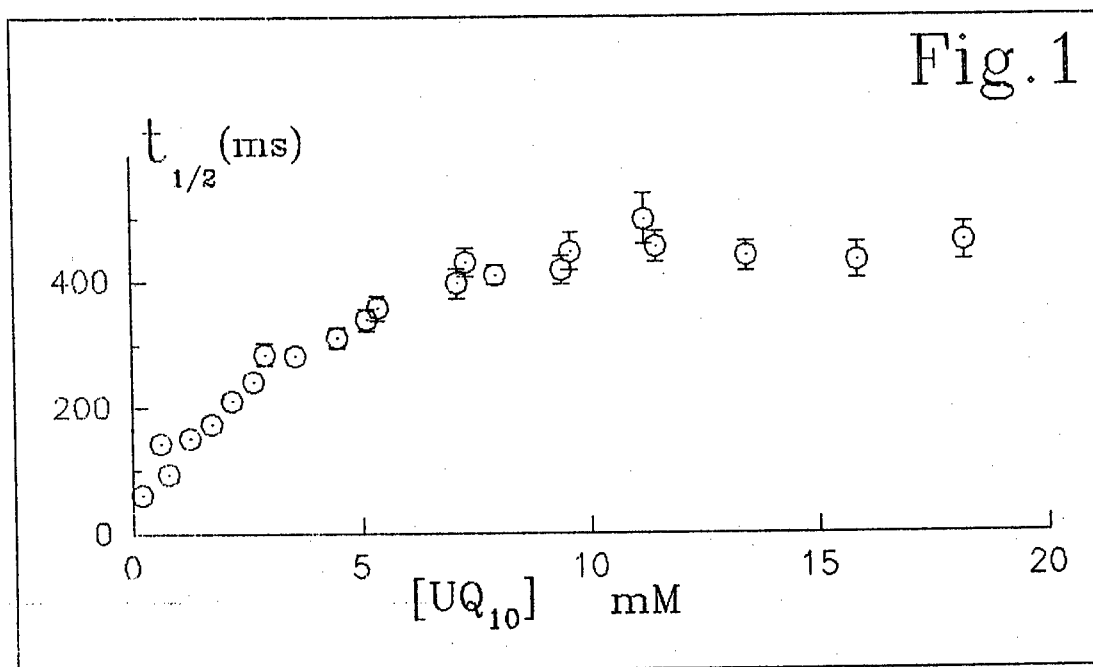
[§] Dipartimento di Biologia, Università di Bologna, Italy

Photosynthetic reaction centers from *Rhodobacter sphaeroides*, strain R-26, have been incorporated in phospholipid liposomes than extracted in hexane as lecithin reverse micelles. The micelles solution containing the reaction centers has been transformed in viscoelastic gel by addition of a large concentration of lecithin and of a critical amount of water (W_0^{crit} , where W_0 indicate the molar ratio between water and phospholipids).

The photochemical activity of the protein was retained in all the system examined.

The kinetics of charge recombination between the primary photo-oxidized electron donor (P^+) of the reaction center and the primary (Q_A^-) and secondary (Q_B^-) quinone acceptors were investigated by time-resolved absorption spectroscopy.

The charge recombination kinetics resulted to be strongly dependent by the organization of the lipidic system employed. On the other side the analysis of flash-generated P^+ decay demonstrated that in all the systems the kinetic of P^+ re-reduction can never fit to an exponential decay and the light-induced charge separation involved always the Q_B site. In the hexane solutions the recombination kinetic of the charge separated state $P^+Q_B^-$ was found to be, strongly, dependent from the concentration of the dissolved quinone.



As shown in Fig.1 the increasing of the quinone concentration results in the increasing of the observed overall half-time of the charge separated state.

In addition in the gel the slow component of the kinetic (attributed to the recombination from $P^+Q_B^-$) was found to be strongly affected by the viscosity of the system.

To account for the multiphasic kinetics observed, multiple conformational states of the reaction center, local heterogeneity of the lipidic systems, and the exchange interaction of the excess quinone with the Q_B binding site have been considered..

The Effect of Sunlight on Some Effervescent Beverages in the Egyptian Market

by

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Effervescent beverages are usually produced in Egypt according to highest universal standards. Some of these beverages, however, are exposed to sunlight during the marketing process. Many sellers-particularly in rural areas-keep these products exposed to sunlight for long periods. This problem prevails in many third-world countries.

In the present study we investigate the effect of sunlight on some of these products .

The colouring dyes in the studied products were identified as sunset yellow E110 and carmoisine. The colouring dye tartrazine has also been studied for comparison. The photostability of these colouring dyes was studied in persence of food acids e.g. ascorbic and citric acids. The major photochemical products are generally identified as the corresponding amines . the photochemical quantum yields (ϕ_c) of these processes have been measured .The transmittance of ordinary containers to sunlight has been studied using chemical actinometry .

The thermal stability of these colouring dyes in the presence of the above-mentioned food acids has also been studied to compare with photostability and to allow for the green-house effect experienced by plastic and glass containers .

**FREE VOLUME SENSING FLUORESCENCE "TICT" PROBES FOR
CYCLODEXTRINS INTERIOR**

K. A. AL-HASSAN

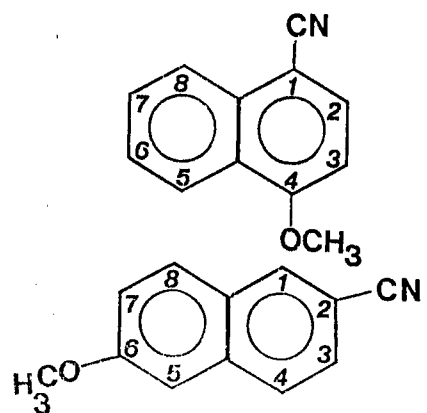
DEPARTMENT OF CHEMISTRY, YARMOUK UNIVERSITY

IRBID, JORDAN

The Influence of Methoxy and Cyano Substituents on the Photocycloaddition of Ethenes to Naphthalenes

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The photocycloaddition of 4-methoxy-1-naphthonitrile and 6-methoxy-2-naphthonitrile with a number of ethenes have been investigated. The reactions produced [2+2] cycloaddition products in all systems. However, the regiochemistry of additions were totally different. 4-Methoxy-1-naphthonitrile gave cyclobutane adducts with ethenes in which the addition has taken place across the 1,2-bond of the naphthalene, whereas 6-methoxy-2-naphthonitrile gave cyclobutane adducts with ethenes in which the addition has taken place across the 5,6-bond of the naphthalene. A possible explanation relating the influence of the substituent versus its position in the ring is reported.



+ Ethenes \rightarrow The [2+2] cycloaddition,
always occur at the 1,2-bond.

+ Ethenes \rightarrow The [2+2] cycloaddition,
always occur at the 5,6-bond.

**PHOTOEXCITATION OF TRANSITION METAL COMPLEXES IN
ORGANIC SUBSTRATES**

S. I. ALI

DEPARTMENT OF CHEMISTRY, JAMIA MILLIA ISLAMIA

JAMIA NAGAR, NEW DELHI-110025

Peculiar Spin Polarization in the Photolysis of Several Ni- and Pt-complexes

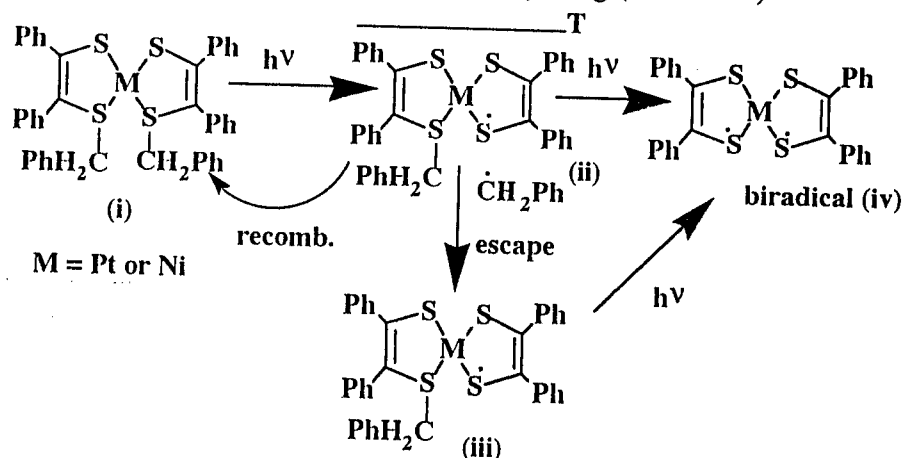
S. S. Ali*, K. Maeda, T. Azumi

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M. Kajitani, T. Akiyama, and A. Sugimori

Faculty of Engineering Science, Sophia University, Japan.

The photolysis of complexes (i) in scheme 1 is known to proceed via the triplet excited state to yield an organic radical and a metal containing radical fragments; c.f. the first step in Scheme 1. The ESR studies reveal that the lifetime of the metal-containing radical is very long (>100 sec.).



Scheme 1

Performing the above photoreaction in an NMR probe led surprisingly to anomalous CIDNP signals for the protons of the solvents (benzene or dichloromethane). Moreover, the polarization persisted for several minutes; c.f. figure 1.

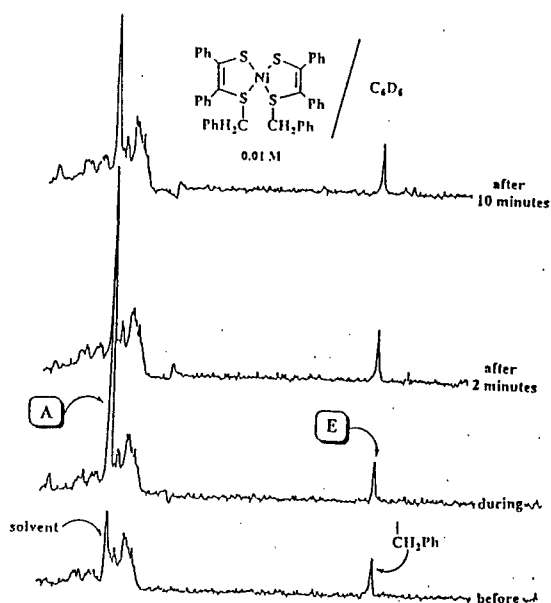
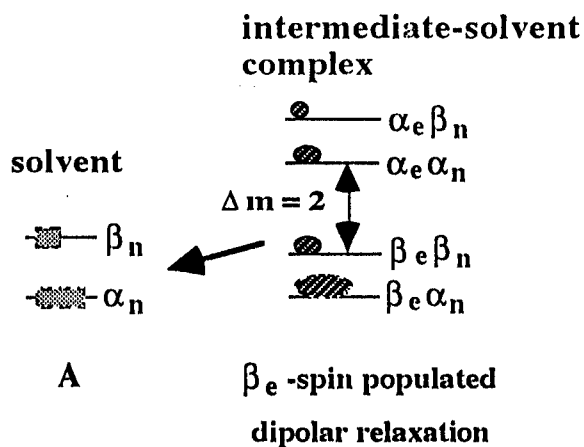


Figure 1

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We interpret the anomalous behavior in terms of electron polarization transfer from an electron polarized intermediate into the nuclear spin of the solvent protons by dipole-dipole interaction induced cross-relaxation mechanism.



This mechanism requires the presence of a very long-lived electron polarized intermediate because the polarization persisted for very long time. A mechanism that can account for the observed polarization will be discussed in the light of the CIDNP results and the laser power dependence of the CIDNP intensities.

The details of the mechanism in which the polarization is created in that intermediate is peculiar at this stage. However, an explanation based on the extension of the radical pair mechanism proposed by Closs [1,2], and another using the triplet-triplet pair encounter [3] will be discussed.

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- [3] N. J. Turro, I. V. Khudyakov, S. H. Bossmann, D. W. Dwyer, *J. Phys. Chem.*, **97**, 1138 (1993).

THE SIGNIFICANCE OF SURFACE STATES FOR PHOTOELECTROCATALYSIS AT THE SEMICONDUCTOR/ ELECTROLYTE INTERFACES

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The surface of semiconductors with a cubic tetrahedral structure is generally characterised by a distribution of dangling bonds, which determine, for instance, the position of the Fermi level. A stabilisation of such surfaces is reached either via reconstruction or relaxation. In spite of these structural stabilisations the surface still reacts towards adsorbates. Unfortunately, this type of semiconductors, e.g. silicon, are poor materials for photoelectrocatalysis, hence the major process is bypassed to photocorrosion products. However, the surface of d-band semiconductors with pyrite structure, e.g. MS_2 ; where $M = Ru, Fe$, are remarkably inert. The pyrite structure is built up by the transition metal atom and S_2 dumbbells forming face-centered cubic (fcc) sublattices. The M atom is coordinated octahedrally by sulphur atoms. The inertness of cleaved (100) RuS_2 surface has been confirmed by scanning tunnelling microscopy (STM) experiments under ambient conditions, where atomic resolution was obtained, as recently reported by our group. Images could also be recorded after leaving the surface exposed to air. The stability of the surface is not only due to the crystal structure but to the electronic structure. However, the scenario can be completely different during photoelectrocatalysis of water oxidation as will be shown in this presentation. Firstly, because the surface of RuS_2 must be activated in order to convey the photogenerated holes to the reaction centres. This means that the interaction of water with the semiconducting surface may change the nature of the species bounded. Secondly, photoelectrocatalysis must then occur efficiently by the presence of a driving force, i.e., an important Helmholtz potential drop at the interface. The validity of the above statements will be discussed in the frame of various experimental evidences such as low temperature photoelectrochemistry, electrochemical impedance spectroscopy (EIS), and ex situ STM.

Deactivation Channels of Multidimensional S_1 State of some Laser Dyes

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The photophysical properties of some donor-acceptor dye molecules such as trans-4-dimethylamino-4'-cyano-stilbene (DCS) and its model bridged derivatives (DCSBD) and (DCSBS) with different degrees of flexibility were investigated.

This work reports the effect of solvent polarity and viscosity on the fluorescence properties including fluorescence quantum yields of the three molecules studied.

The results lead to the conclusion that cis/trans isomerization (or double bond twisting) in the excited singlet state is the most important nonradiative deactivation channel to the ground state.

Moreover, results are presented suggesting formation of Dye-protic solvent exciplexes. The equilibrium constants of exciplex formation (of 1:1 stoichiometry) were determined by using stationary fluorescence technique.

Furthermore, torsional relaxation behaviour, as reflected in the fluorescence quantum yield, is correlated with solvent viscosity/free volume.

Acknowledgement: The compounds are courtesy of Dr. *Rafik O. Loutfy*.

Energy transfer by electronically nonadiabatic transitions *

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The detailed mechanism which governs the redistribution of energy stored in a molecule when it encounters other species relies on the modalities of electronic nonadiabatic transitions.

In this presentation, recent experimental and theoretical progress is reported both on the proper representation of potential energy surfaces involved in nonadiabatic processes and on the formulation of the dynamics for the transitions. A few specific examples are discussed.

Although some features of potential energy surfaces relevant for inelastic and reactive molecular encounters can be obtained by quantum chemical calculations, the basic ingredients for their mapping are empirical, and rely on results from spectroscopic and molecular beam scattering techniques. Semiempirical correlation rules [1] allow characterization of features to the level of accuracy which is needed for the dynamics.

In turn, the dynamics requires development of formulas for transition probabilities which go beyond classic formulas, such as the Landau-Zener, to include tunneling and interference effects [2].

A further important aspect is the need of separating time scales for electronic transitions and redistribution of vibrorotational modes.

Examples from our work include the selective electronic energy transfer from a rare gas to nitrogen [3], the role of the vibronic manifold

in an ion molecule reaction [4], and propensities for vibrational excitation in positive ion-negative ion recombination [5].

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- 5) V. Aquilanti, R. Candori, S.V.K. Kumar and F. Pirani, to be submitted;

* Presented at 3rd International Conference on Solar Energy Storage and Applied Photochemistry, Cairo, Egypt, 8-14 January 1995

Studies of photochemical reactions by nuclear-spin-polarization-detected ESR spectroscopy

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The initial step of most of chemical reactions in solution is the formation of radical pair. The radical pair may either recombine to a recombination product or dissociates into free radicals. The fate of the whole reaction path is governed by the small interaction in the radical pair. Therefore, in order to fully understand chemical reaction, it is important to somehow observe the spectrum of radical pair. However, in most of conventional spectroscopy (electronic spectroscopy and ESR), it is almost impossible to distinguish between radical pair and free radical.

The nuclear-spin-polarization-detected ESR spectroscopy developed recently is a devise to detect the spectrum of radical pair separately from the free radical. The method is based on the detection of the effect of the microwave on the intensity of nuclear polarization (or CIDNP) of a reaction product. The spectrum consists of two parts: SNP (stimulated nuclear polarization) and DNP (dynamic nuclear polarization). The SNP component corresponds to the ESR spectrum of radical pair, and the DNP component corresponds to the ESR spectrum of free radical.

We have further developed this method to time-resolved manner. By this method one can analyze the time developing of radical pair and free radical independently.

A New Diolefinic Laser Dye : 2,5 - Bis - 2- (2- Naphthyl) Vinylpyrazine (B2NVP)

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(Department of Chemistry , Faculty of Science , Tanta Univ., Tanta , Egypt)

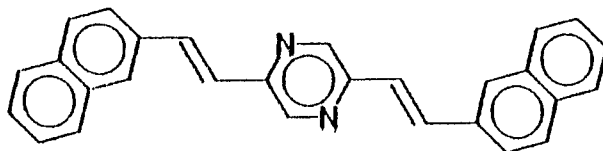
A.S. Babaqi

(Department of Chemistry , Faculty of Science , Sana'a University, Sana'a , Yemen) , and

M. Klink, J. Sauter and E. Daltrozso

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The titled dye acts as a laser dye upon pumping with nitrogen laser ($\lambda_{ex} = 337.1$ nm). B2NVP solutions in dimethylformamide give amplified spontaneous emission (ASE) maximum at ca . 495 nm . The excited state absorption (ESA) occurs at around 500 nm . This excited state absorption inevitably reduces the laser efficiency of this dye .



(B2NVP)

B2NVP has a short excited state lifetime (1.28 ns) and a low photochemical quantum yield (ϕ_c) of 2.6×10^{-4} . The dye undergoes solubilization in both anionic and cationic micelles with subsequent increase in emission efficiencies .

Emission spectra at different excitation wavelengths reveal the possible existence of rotomers arising through non-free rotation around the $\text{C}_{\text{ethylenic}} - \text{C}_{\text{naphthyl}}$ sigma bonds

TREATMENT OF WASTEWATER FROM REFINERIES BY OZONE /UV CATALYTIC PHOTOXIDATION

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A. M. EL-Sabbagh*

Egyptian Petroleum Research Institute *, Nasr City- Cairo, Ain Shams
University, Faculty of Science, Department of Biochemistry**
National Research Centre, Chemical Engineering and Pilot Plant
Department***, Dokki, Cairo Egypt

Laboratory studies concerning treatment of wastewater from Cairo ,
refinery , Mostorod are presented .

Chemicaal oxidation of samples contaning emulsified oil using catalytic
ozonation combined with ultraviolet light is evaluated.

Fe(III) tetracarboxyphthalocyanine at a concentration of 2% based on
emulsified oil in wastewater was added to synthetically prepared sample
befor the treatment with gaseous ozone at doses of 80-500 mg/L and
applying U. V. Light (15watt).

The treated water was followed by filtration. Effeciency of combined catalytic
and ozonation process reached 99.7% using turbidimetric technique.

This work was adopted from the Ph.D. Thesis of Sh. El-Rafei

Photolysis and Thermolysis of Acidamide and Sulphonamide Derivatives

By M. Z. A. BADR.

Faculty of Science, Assiut University, Assiut Egypt.

Ultraviolet irradiation and pyrolysis products and mechanisms will be discussed for N-acetyl derivatives of arylamides, hydroxamic acids, and N-sulphonamides and N-sulphohydroxamic acids.

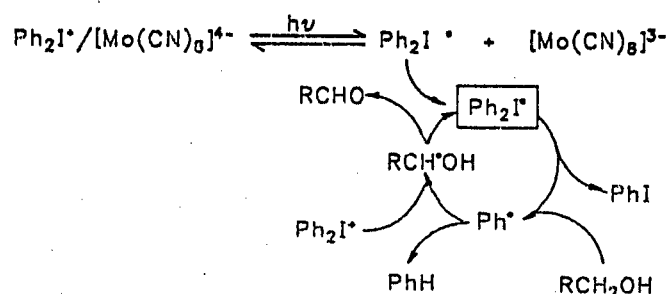
Homolysis mechanisms and free radical reactions pathways will be discussed.

SELECTIVE OXIDATION OF ALCOHOLS BY DIPHENYLIODONIUM IONS IN A PHOTOINDUCED CHAIN REACTION

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Universität Leipzig, Institut für Anorganische Chemie, D-04103 Leipzig, Germany

Solutions of diphenyliodonium salts and easily oxidizable cyanometalates, $[\text{Mo}(\text{CN})_8]^{4-}$ e.g., exhibit long-wavelength ion pair charge-transfer (IPCT) absorption bands. Irradiation into the IPCT spectral region causes photo-redox reactions with primary quantum yields close to unity. The diphenyliodol radical as one of the photoproducts immediately decomposes to give iodobenzene and a phenyl radical. In the presence of primary or secondary (but not tertiary) alcohols this radical acts as a chain carrier in the oxidation of alcohols by diphenyliodonium ions present in excess (see Scheme). Turnover numbers of several thousands, depending on the nature of substituents, reactants' concentrations and the absorbed light-intensity, have been observed. The chain reaction is terminated by radical combination reactions yielding biphenyl and R-CH(Ph)-OH .



Using terpene alcohols as substrates and $\text{H}_2\text{O}/\text{tert.}-\text{Butanol}$ (50/50) as the solvent neither double-bond isomerization nor racemization are observed. Citral a (Geraniol), but no citral b (Neral), is obtained from geraniol, e. g. After optimization of the reaction conditions the aldehydes have been obtained with more than 90% yield in the ten gram scale.

HOMOGENEOUS SOLAR DETOXIFICATION OF CONTAMINATED WATER

by

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The use of sunlight to stimulate the detoxification of contaminated ground waters is an attractive goal, since it eliminates the need for large amounts of electrical energy now used commercially in the destruction of pollutants using ultraviolet light. These processes are generally called *Advanced Oxidation Processes* (AOPs) and involve the generation of reactive radicals, such as the hydroxyl radical, which then react with and degrade organic pollutants. Unfortunately, the ultraviolet processes in use today require UV light below 300 nm, which is not available in terrestrial sunlight.

Titanium dioxide (in its anatase crystalline form) does have some ability to degrade pollutants using sunlight and there has been a considerable amount of research and even a field demonstration.

Solarchem has developed a new process called Solaqua® (patent issued¹), which absorbs light out to 500 nm and thus is able to absorb almost 18% of the solar spectrum. The process generates hydroxyl radicals with a high quantum yield, so the chemistry is very similar to that in UV/peroxide treatments. In parallel solar experiments Solaqua® has shown the ability to degrade organic pollutants at over 50 times the rate for the heterogeneous titanium dioxide process.

The absorber in Solaqua® is the ferrioxalate ion, which has been used extensively as an actinometer. The ferrioxalate photochemical reaction generates ferrous ions, and in the presence of hydrogen peroxide (the Fenton reaction) hydroxyl radicals are generated, which then attack and oxidize almost all organic pollutants.

The presentation will outline the experiments we have conducted to optimize the process, to measure quantum yields and to explore reactor designs. Some aspects of the mechanism will be discussed.

Part of this work was carried out under a Research Contract with the U.S. National Renewable Energy Laboratory.

1. Safarzadeh-Amiri, A., "Photocatalytic Method for Treatment of Contaminated Water", US Patent No. 5,266,214, Nov. 30, 1993.

* Dr. Bolton is also (1/2 time) a Professor of Chemistry at The University of Western Ontario, London, Ontario, Canada.

The Mechanism of Early Events in Photosynthesis

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The initial energy and electron transfer processes in photosynthetic reaction centers (RCs) are of interest to anyone interested in photochemistry, including possible applications in solar energy conversion, non-linear optics and optical information storage and processing. Despite many years of effort and a high resolution x-ray crystal structure of the RC, the mechanism of the earliest processes remain uncertain and the subject of great controversy. Two key questions have emerged: (i) does the earliest charge separation process take place in one or two steps, and is this concept meaningful given the very short time scale? and (ii) even though two structurally similar electron transfer pathways exist in the RC, only one is used; what is the molecular origin of this unidirectional electron transfer?

Our research combines ultra-fast spectroscopy, electric field perturbations and protein manipulation by recombinant DNA techniques. Using very short laser pulses, we have observed oscillations in the fs/ps spontaneous fluorescence from the special pair primary electron donor whose excited states initiate photosynthesis. This demonstrates that the excited state is not at thermal equilibrium during the initial electron transfer reaction. Using Stark spectroscopy we have discovered that the excited state of the special pair is highly polarizable and is very sensitive to local electrostatic fields within the protein. These fields can be changed by altering amino acid residues which make hydrogen bonds with the special pair. Stark spectroscopy can also be used to calibrate the sensitivity of different chromophore absorption bands in the RC to transient internal electric fields created during charge separation. This has recently been used to demonstrate that the average dielectric screening on the functional side of the RC is several times larger than on the non-functional side, likely making a significant contribution to unidirectional electron transfer. Finally, we have been able to explore the mechanism of the initial long-distance electron transfer reaction using electric fields to perturb the reaction. This provides a convenient approach for tuning the energy of charge separated intermediates, and is sensitive to the orientation of the electric dipole moments associated with these intermediates. By performing this experiment on the fs/ps time scale it is possible to distinguish the one and two step mechanisms.

TIME-RESOLVED PHOTOTHERMAL MEASUREMENTS ON BIOLOGICAL PHOTORECEPTORS

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Molecular movements in the microsecond range taking place after laser-pulse excitation of various photoreceptors (bacteriorhodopsin, rhodopsin, phytochrome, the photoactive yellow pigment, and photosynthetic units and reaction centers) have been analysed using temperature-dependent laser-induced optoacoustic spectroscopy (LIOAS). Studies with chromophore model compounds (isomerizable carbocyanines as models for the isomerizable chromophores in phytochrome and in the retinal proteins, and photoinduced charge transfer reactions as models for the photosynthetic units) indicate that the movements should be interpreted as arising from changes in the location of solvent molecules around a phototransformed chromophore with different dipole moment than that of the parent chromophore. Therefore, the volume changes in the chromoproteins (in some cases contractions and in other cases expansions) are interpreted as changes in the immediate protein environment of the respective chromophore, due to photoinduced dipole moment changes after light absorption. These volume changes, reflecting a density change concomitant with the photoinduced transformation, together with the time-resolved calorimetric information derived also from the photothermal measurements, yield new information about the chromophore-protein interactions in each photoreceptor. Photothermal beam deflection (PBD) after pulse excitation permits the analysis of molecular movements up to hundreds of milliseconds, the time range related to the biological signal transduction. Using PBD with polarized excitation and detection together with linear dichroic measurements with the membrane patches of bacteriorhodopsin, it has been possible to time resolve the photoinduced movements (as well as to estimate the stepwise enthalpy changes) for the complete photocycle in this retinal protein.

Intersystem Crossing in Organic Triplet Intermediates.

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The University of Texas at Dallas*

Intersystem crossing from triplet to ground state surfaces at configurations at which the two approach relatively closely energetically is a critical step in nearly all triplet state photochemical reactions, and in most chemically useful cases is controlled by SOC. We have studied alkene triplets and triplet biradicals (1) by conventional organic mechanistic work to determine the chemical outcomes and infer the identity of intermediates; (2) by laser flash photolysis to determine (a) transient lifetimes which often will equate to intersystem crossing (ISC) rates, (b) energies of transients (by time-resolved photoacoustic calorimetry), and (c) other physical and kinetic properties of the transients; and (3) by CAS-MCSCF computations of spin-orbit coupling (SOC) in small model species. Our objective is a fundamental understanding of triplet biradicals and olefin triplets, specifically their energetics and energy surfaces, conformations, dynamics (especially ISC rates), and ultimately the role of all these in determining the outcomes of photochemical processes. We believe that our results show that we largely understand the ISC process at that level now. Recent work suggests that nonbonded interactions may play a much more general role in ISC than has been hitherto believed, a point which deserves further exploration.

Dye Molecules in Zeolites as Artificial Antenna*

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When cationic dye molecules are exchanged into the parallel channels of L zeolite, they are so close together that energy transfer can occur. The restricted geometry of the L zeolite channels excludes aggregation and self-quenching even at very high concentrations. We report three types of experiments with pyronine and oxonine which exhibit that such a zeolite dye system fulfills basic needs of an antenna. First, we show that energy transfer occurs inside of the zeolite microcrystals filled with a mixture of both chromophores. This proves that the achieved distance distribution fulfills the conditions imposed by the law of electronic excitation energy transfer. Second, we show that all the quanta absorbed by pyronine inside of the zeolite microcrystals can be trapped by a quencher or by a luminescer with the right spectral properties placed on their surface. In the third experiment we show that in a mixture of zeolite microcrystals loaded with pyronine as donor and such loaded with oxonine as acceptor A, energy transfer occurs from the D to the A filled particles.

*G. Calzaferri and N. Gfeller, *J. Phys. Chem.* 96 (1992) 3428.

F. Binder, G. Calzaferri and N. Gfeller, Tenth International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-10), Interlaken, Switzerland, Book of Abstracts, G. Calzaferri (Editor), 1994, p. 109-110.

F. Binder, G. Calzaferri and N. Gfeller, *Chimia* 48 (1994) 292.

F. Binder, G. Calzaferri and N. Gfeller, *Solar Energy Materials and Solar Cells*, (1995) in the press.

The two processes of light collection and its conversion to chemical/electrochemical energy are separated from each other, in natural photosynthesis. The light is absorbed by an antenna consisting of 300-1000 chlorophyll molecules arranged as monomers in a protein environment. This allows very fast energy transfer from an electronically excited molecule to its unexcited neighbor, the time scale being in the order of one ps. The excitation energy is transported by this mechanism to the reaction center, where charge separation occurs. This is a very efficient process which should be considered in the research of artificial photosynthesis systems.

Experiments for controlled transfer of excitation energy through thin layers based on the Langmuir Blodgett technique have been described many years ago by Hans Kuhn and coworkers. Current attempts of Balzani et al. to construct artificial antenna based on linking molecular components by covalent or coordination bonds have been remarkably successful. The obtained supramolecular dendritic structures of nanometer size are impressive and inspiring. We have taken a different approach by using the three-dimensional highly ordered network of zeolites as a framework to build an antenna. The idea behind this approach is that the ordered pore and channel structure of the zeolite can be filled with appropriate dye molecules so that the packing is dense enough to fulfill the needs of fast Förster type energy transfer but that each dye molecule still acts as a monomer. The necessary condition of the arrangement is, that energy transfer from an excited molecule to an unexcited neighbor is much faster than any other process. An appealing zeolite/dye system to investigate this idea experimentally is L zeolite and dyes such as thionine, oxonine, pyronine, proflavine and

structurally related molecules as illustrated in Figure 1. The photophysical and photochemical behavior of organic dyes in zeolites has currently become of increasing interest. We have studied the isothermal ion exchange of thiazine dyes in L zeolite and we have found that thionine enters the large cavities, as shown in Figure 1, while at room temperature the somewhat larger alkylated analogs of thionine, methylene blue and ethylene blue remain on the surface of the microcrystals where they form dimers and higher aggregates.

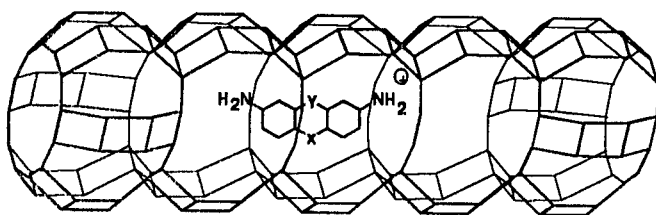


Fig 1. Schematic view of a dye molecule in the main channel of L zeolite and structure of some cationic dyes capable to enter this channel.

The high absorption coefficients of pyronine and oxonine and their spectral properties make them good candidates for constructing

an antenna. Furthermore the restricted geometry of the channels prevents the formation of aggregates inside of the zeolite, even for concentrations up to 0.2 M with respect to the zeolite volume. This has to be compared with the tendency of aggregate formation in aqueous solutions where it starts already at about 10^{-5} M.

We describe three types of experiments to test if such a zeolite/dye arrangement fulfills basic needs of an antenna. First we must find out if energy migration occurs inside of the zeolite microcrystals filled with chromophores. This will only be the case if the distance distribution fulfills the conditions imposed by the law of electronic excitation energy transfer. Intercalation of a mixture of two dyes D and A with the right spectral properties is a possibility to test this, as schematized on top of Figure 2. If the energy migration is efficient, it should be possible to

trap all the quanta absorbed by D inside of the zeolite microcrystals by fixing a luminescer A or a quencher with the right spectral properties on its surface as illustrated in the middle of Figure 2. On its bottom we mix zeolite microcrystals loaded with dye D and such loaded with dye A, to find out if energy transfer occurs from the D to the A filled particles. Pyronine as D and oxonine as A are dyes which fulfill the spectral and the stability conditions needed for such experiments and they are therefore investigated.

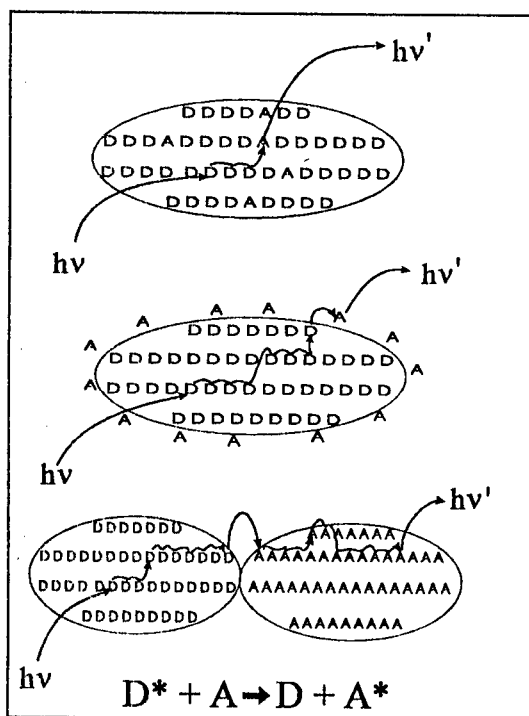


Fig. 2. Representation of energy migration and energy transfer in the three spatially different Donor-Acceptor (D-A) arrangements. Top: D and A, are located in the same zeolite microcrystal. Middle: D is inside of the zeolite and A is attached at its outer surface. Bottom: Mixture of dye loaded zeolite microcrystals, each containing only one type of dye.

DYNAMICS OF BARRIERLESS STRUCTURAL RELAXATION OF
EXCITED PYRIDYLOXAZOLE CATIONS

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The structural relaxation of excited 2-(3-pyridyl)-5-phenyl-oxazole cation (3PyPOH^+) and its N-methylated analog (3PyPOMe^+) in various solvents has been studied. In low viscous solvents at room temperature the fluorescence of 3PyPOH^+ and 3PyPOMe^+ cations is characterized by the anomalous Stokes shift (190 nm in EtOH) and low quantum yield. The fluorescence intensity depends slightly on solvent polarity. As solvent viscosity increases the fluorescence intensity increases and shortwavelength shift takes place. The anomalous fluorescence Stokes shift and its dependence on solvent viscosity point out that the fluorescence takes place from the continuum of intermediate states. In low viscous solvent the picosecond fluorescence kinetics does not depend on the emission wavelength. At moderate solvent viscosity the fast fluorescence decay at the shortwavelength side and the fast fluorescence rising at the longwavelength side of the spectrum are observed in the picosecond time domain.

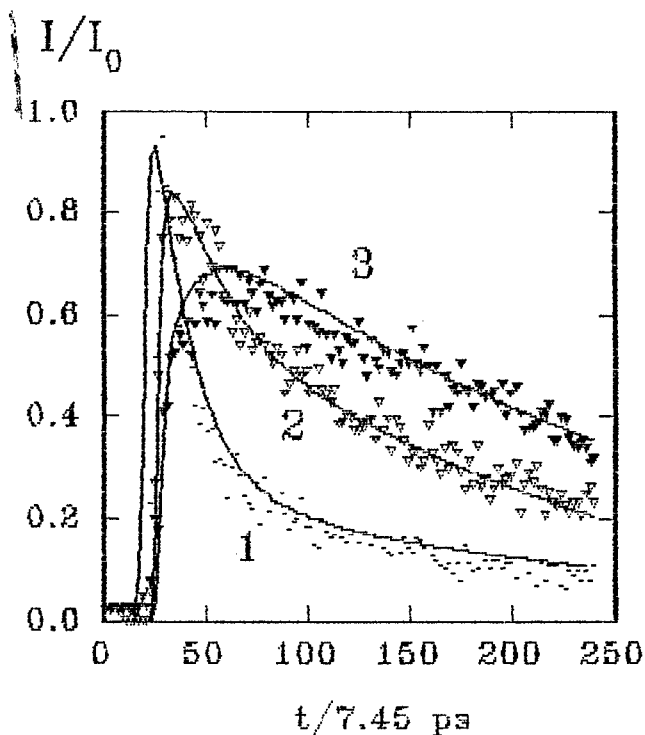
Effective radiative rate constant (k) has been estimated from fluorescence quantum yield and lifetime. At constant viscosity k is practically independent of the temperature. The value of k increases about 5 times as one goes from nonrigid to rigid matrices. The fluorescence maximum wavelength and k are changed simultaneously. The dependence of k on the alcohol viscosity allows to conclude that in the excited state structural relaxation consisting in the rotation of pyridinium ring relative to oxazole one takes place. In excited cation the equilibrium angle between pyridinium and oxazole fragments is greater than that in the ground state. At comparable values of

the structural relaxation time and lifetime of the excited state the fluorescence arises from continuous set of non-equilibrated intermediate states with various torsional angles between pyridinium and oxazole rings and hence with different values of k .

The structural relaxation dynamics is described by the model according to which the relaxation is a molecular motion on excited state harmonic surface in friction forces field. It is assumed that temporal evolution of excited state population density is described by modified Smoluchovski equation. The calculation has been made taking into consideration the normal distribution of photophysical elementary constants on relaxation coordinate (x). It is supposed that the fluorescence spectrum has the same profile (gamma-distribution) for different x . This model satisfactorily fits fluorescence kinetics data over the whole spectrum (Figure) and fluorescence spectra of studied systems in wide temperature range.

Figure.

Experimental and calculated fluorescence kinetic curves of 3PyPOH⁺ in glycerol at 20833 (1), 16667 (2) and 19231 (3) cm⁻¹ emission wavenumbers at 308 K.



REGIO- AND STEREOSELECTIVITY IN LIGHT INDUCED [4+2]-CYCLOADDITIONS OF α -CYANOENAMINES TO AROMATIC CARBONYL COMPOUNDS, NITRILES AND HYDROCARBONS

Dietrich Döpp

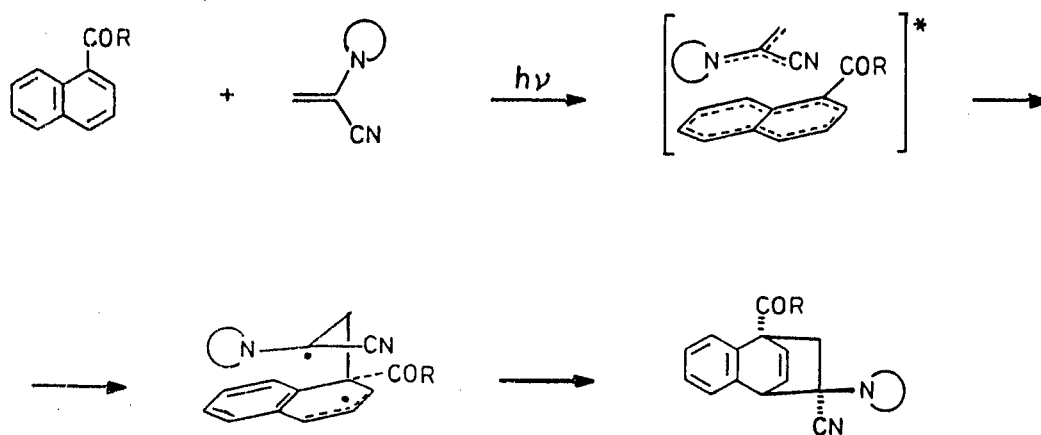
Fachgebiet Organische Chemie, Gerhard-Mercator-Universität - GH Duisburg,
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α -Cyanoenamines, as other captodative (c,d-) [1] alkenes, bear a donor and an acceptor at the same terminus of a double bond. This unique substitution pattern makes the double bond radicophilic [1] and at the same time enhances the olefin's aptitude for complexation with suitable electronically excited reaction partners.

In a stepwise photocycloaddition involving a c,d-alkene, the reactant may form an oriented exciplex and, as a result of the first bond forming event, a 1,n-bi-radical may result which

- features one especially stabilized [2] c,d-terminus contributing to its over-all stability,
- may experience intramolecular attractive or repulsive interactions influencing the relative stabilities of selected conformations.

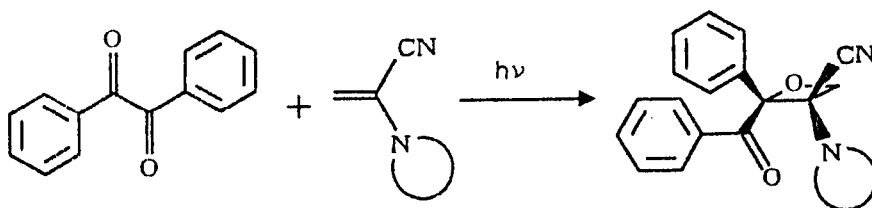
Thus product connectivity and structure may result from selection on two levels [3] (exciplex and biradical), as exemplified for the 1,4-photocycloaddition to acynaphthalenes [4]:



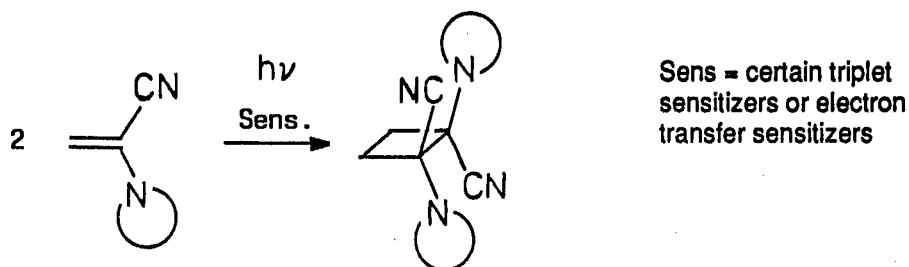
Other fields, in which high regio- and stereoselectivities have been observed:

[2+2]-Photoaddition of c,d-olefins to 1-naphthonitrile [5],

Paterno-Büchi-reactions of c,d-olefins with benzil type diketones [6]:



[2+2]-Photodimerization of α -cyanoenamines [7]:



Other [2+2] additions, but with reduced stereo- and diastereoselectivity, respectively, are found in the light induced additions of α -cyanoenamines to acenaphthylene and naphthalene.

Acknowledgement: Generous support of our work by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

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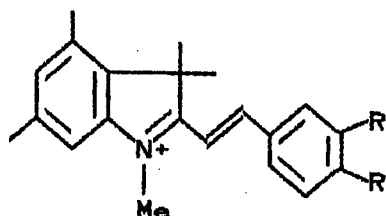
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- [2] For recent reliable quantifications, see: R. Schulze, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1993**, *126*, 1031; F. Weller, S. P. Verevkin, M. Keller, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1994**, *127*, 697.
- [3] H. Buschmann, H.-D. Scharf, N. Hoffmann, M. W. Plath, J. Runsink *J. Am. Chem. Soc.* **1989**, *111*, 5367.
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- [6] Planned doctoral thesis by M. A. Fischer, University of Duisburg.
- [7] Doctoral thesis by J. Bredehorn, University of Duisburg, 1994.
- [8] Planned doctoral thesis by J. Weber, University of Duisburg.

EXCITED STATE RELAXATION PROCESSES OF CROWNED STYRYL DYES AND THEIR METAL COMPLEXES

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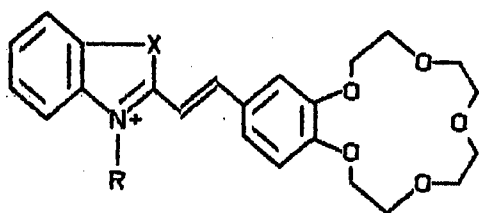
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The photophysics of crowned styryl dyes (I) and their com-



Ia: R = H

Ib: R = OMe



Ic: X = CMe₂; R = Me; 5,6-Me₂

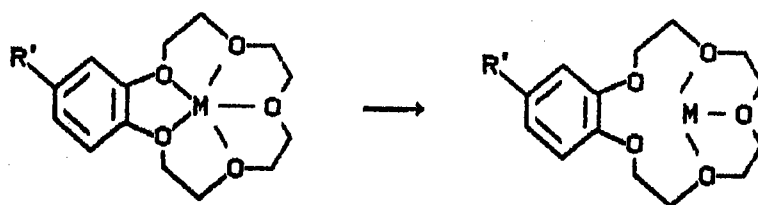
Id: X = S; R = Et

Ie: X = S; R = Et; 5-MeO

If: X = S; R = Et; 4,5-CH=CHCH=CH

plexes with sodium cation in EtOH has been studied. The complexation of Ic, Id, Ie, If with Na⁺ results in blue shift ($\Delta\nu_a \approx 700 \text{ cm}^{-1}$) of absorption spectra (Table). This shift of Ia and Ib without macrocycle in the presence of NaClO₄ is less considerably and caused by salt effect. The fluorescence spectra of Ic, Id, Ie, If with Na⁺ are shifted to high frequencies ($\Delta\nu_f \approx 150 \text{ cm}^{-1}$ at -100 °C) but in considerably less extent (Table). The fluorescence excitation spectrum of styryl dye with Na⁺ coincides with absorption spectrum of complexed form and differs from absorption spectrum of the initial form. It points out that the adiabatic reaction in excited state takes place.

The results obtained are consistent with the model of metal recoordination in excited state. In excited state the coordination bonds of metal ion with oxygen atoms of pyrocatechol fragment are weakened:



Such bond change is caused by charge transfer from pyrocathol fragment to heterocycle one.

The fluorescence quantum yield (ϕ) of styryl dyes increases dramatically as the temperature decreases. The barrier height of radiationless deactivation (3.8, 4.2, 4.2 kcal/mol for Ib, Ic and IcNa⁺ respectively) is close to activation energy of EtOH viscous flow (3.7 kcal/mol). The influence of cation electrostatic field on photophysics of styryl dyes at low temperatures has been discussed.

Table

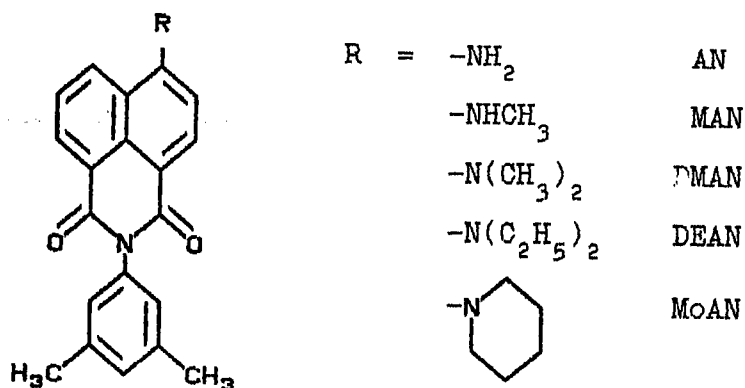
	$\nu_a,$ cm^{-1}	$\Delta\nu_a,$ cm^{-1}	$\nu_f,$ cm^{-1}	$\Delta\nu_f,$ cm^{-1}	ϕ_I -100	$\phi_{I\text{Na}}$ °C
Ia	25820	-170	18740	-70	0.012	0.011
Ib	22360	30	18350	130	0.10	0.12
Ic	22210	670	17960	150	0.30	0.22
Id	23130	840	19260	140	0.38	0.23
Ie	22580	760	18840	-210	0.54	0.17
If	22630	750	18490	50	0.55	0.18

TICT-STATE FORMATION DYNAMICS IN N-ALCOHOLS:
N,N-DIALKYLAMINONAPHTHALIMIDES

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It is assumed that TICT-state formation reaction is accompanied by internal rotation and charge-transfer processes. In this case the strong dependence of TICT-state formation rate on the viscosity and polarity of medium should be observed. In present work the influence of these factors on TICT-state formation rate in N,N-dialkylaminonaphthalimides is investigated.



Fluorescence quantum yield (ϕ) of amino- and N-methylaminonaphthalimides depends slightly on temperature and solvent ($\phi = 0.50 - 0.98$). The fluorescence quantum yield and lifetime of N,N-dialkylaminonaphthalimide considerably decrease as the temperature increases or as solvent polarity and viscosity decrease. This is due to the increasing of radiationless rate constant (k_d), but not to the change of radiative rate constant (k_f). It is supposed that temperature-activated radiationless deactivation in N,N-dialkylaminonaphthalimide is associated with the formation of nonfluorescent twisted charge transfer state (TICT-state), formed by the rotation of dialkylaminogroup relative to the naphthalimide ring plane. In this case the rate constant of TICT-state formation (k_t) is related

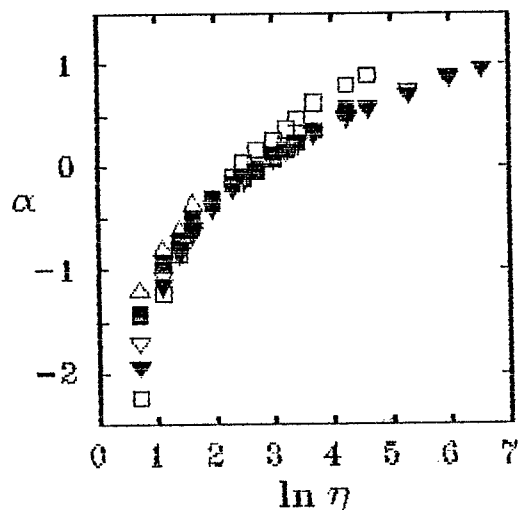
with ϕ by the following equation: $k_t / k_r = 1/\phi - 1/\phi_0$, where ϕ_0 - fluorescence quantum yield from initial state without reaction.

The dependence of k_t on the temperature ($170 < T < 330$ K) and solvent viscosity ($0.5 < \eta < 700$ cP) for DMAN in n-alcohols is quantitatively described by the following expression

$$k_t = k_0 \eta^\alpha \exp(-E/RT)$$

Parameter α is a measure of the viscosity influence on the rate of internal rotation. The activation energy E depends on solvent polarity. To estimate this effect it is assumed that E linearly depends on solvent polarity parameter $E_T(30)$. Temperature dependence of $E_T(30)$ has been taken into consideration. The models using independent or viscosity-influenced α are discussed.

The Arrhenius plots for TICT-state formation rate constant reduced to the same solvent viscosity and polarity for DMAN in different alcohols coincide with each other. The activation energy of TICT-state formation in nonpolar solvents is equal to 9.1 kcal/mol. At viscosity less than 10 cP the rate constant of TICT-state formation depends on solvent polarity and is not affected by solvent viscosity. Solvent viscosity influences markedly k_t constant at viscosity higher than 10 cP. The effect of N,N-dialkylaminogroup size on TICT-state formation rate constant is considered.



Molecular and Supramolecular Systems in Photochromism - Dihydroindolizine a versatile Molecule

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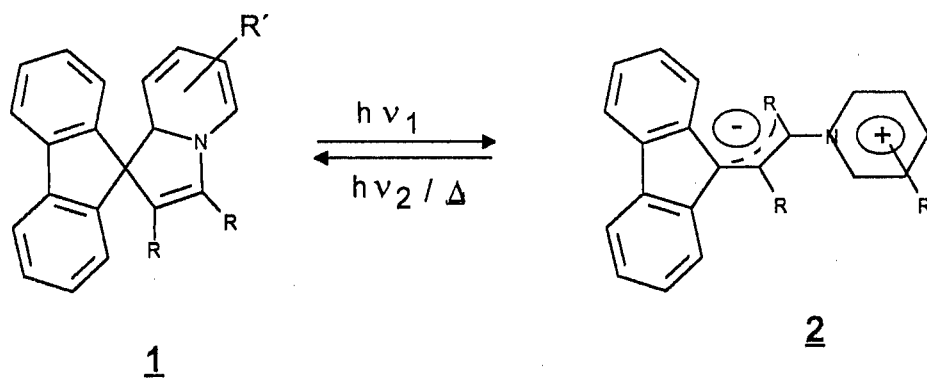
The field of photochromism is receiving more and more interest in the recent past. The development of commercially usable photochromic lenses¹ has given a tremendous impetus to the basic research of photochromes². The extension of the fundamental findings to supramolecular systems opens an additional facet of this research area.

In this talk a survey of the known photochromic systems is given first.

The preparation of dihydroindolizines (DHI) **1** and their photochromism leading to colored betaines **2** based on a 6π - pericyclic reaction, is presented². This class of molecules are π - isoelectronic to spiro-pyrans and -oxazines, which have been studied in great detail. However DHIs **1** show intrinsic differences to the latter, which is reflected in their properties. The mechanism of the photoreaction is elucidated and rate constants of the deactivation channels are presented.

Photoswitchable systems being based on CN-DHIs are shown. Their photochemical reversibility and the photostability is dependent on both substituents and environment.

Linking polyethers to the DHI-molecules affords a new photochromic system allowing for host-guest chemistry. Molecular recognition of metal ions is possible even with binding sites of low efficiency. The selectivity of these podate-DHIs with regard to tuning of reactivity or excited state properties is demonstrated. In a final section a few selected applications, some commercially being used, are shown.



R = H, Alkyl-etc.

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2) H.Dürr, H.Bouas-Laurent, Photochromism - Molecules and Systems, Elsevier, Amsterdam, 1990.

**The Emission Characteristics and Photostability of
1,4 - Bis [β - (2-benzoxazolyl) Vinyl] Benzene (BBVB) and
1,4 - Bis [β - (2-Quinolyl) Vinyl] Benzene (BQVB) .**

by

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(*Department of Chemistry , Faculty of Science, Tanta Univ., Tanta,Egypt*) ,

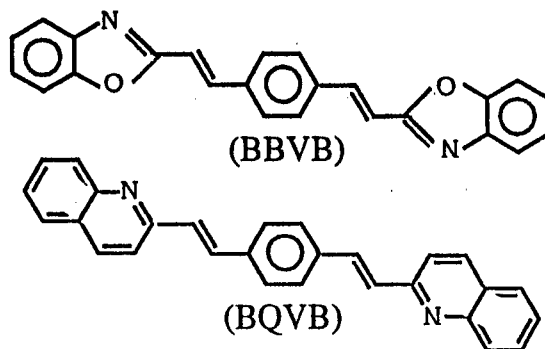
E . M . Vernigor

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Sadovaya 1 / 4 , 103787 , Moscow , Russia*) , and

E . Daltrozzo

(*Fakultät für Chemie , Universität Konstanz , Germany*)

The emission of the titled dyes has been studied in different media including organic solvents as well as micellar and microemulsion media . Both dyes exhibit high fluorescence quantum yields (ϕ_f values around 0.5 depending on the solvent used) . An investigation of their laser activity is underway .



The photostability of these dyes has been studied upon nitrogen laser pumping as well as towards ordinary uv - irradiation ($\lambda_{ex.} = 337$ and 365 nm) . The photochemical quantum yields (ϕ_c) in different media have been measured and , unfortunately, been found relatively high (ϕ_c around 0.01 depending on the medium) .

The effect of medium acidity and basicity on BBVB and BQVB emission and electronic absorption spectra are also reported .

The Emission , Photostability and Complexation Ability of Tetraphenylporphyrin (TPP)

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(* Department of Chemistry , Faculty of Science , and ** Department of Chemistry , Faculty of Education ,
Tanta University ; Tanta , Egypt) .

The emission and electronic absorption spectra of TPP in the presence of Hg^{2+} , Sn^{2+} and Co^{2+} have been studied in organic solvents and in micellar media . A fast complexation process is observed upon allowing TPP to react with Hg^{2+} or Sn^{2+} . This fast reaction has been followed kinetically using stopped - flow technique . The activation parameters of the complexation process have been evaluated .

The fast formation of Hg TPP complex is subsequently followed by complex dissociation that is substantially enhanced by the addition of cationic micelles . The rapid dissociation of Hg TPP in cationic micelles has been studied using stopped - flow technique .

Contrary to the fast reactions between TPP and both Hg^{2+} and Sn^{2+} , the reaction between TPP and Co^{2+} is far slower . Cobalt ions used in complexation with TPP were applied in two forms namely the hexa-aque $[\text{Co} (\text{H}_2\text{O})_6]^{2+}$ and the tetrahedral structure $[\text{Co Cl}_4]^{2-}$. The effect of water addition on Co TPP complex is highlighted .

The photostability of TPP has been studied in some organic solvents and in microemulsion media .

LASER-INDUCED DISSOCIATION OF ORGANIC IODINE GASES:-

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Submitted to the International Conference on Solar Energy Storage and Applied Photo Chemistry to be held January 1995, Cairo - Egypt. Ain Shams Univ.

ABSTRACT :

Measurement of iodine atoms in the plasma of organic iodine gases subjected to laser radiation, was carried out. Laser induced dissociation of the gases was observed. Threshold laser intensities were determined for conditions of dissociation at different laser wavelengths and different laser fluences. Measurement of atomic iodine distribution was then performed using spectroscopic and plasma imaging techniques . Results were elaborated in view of the use of organic iodine gases in the solar laser project.

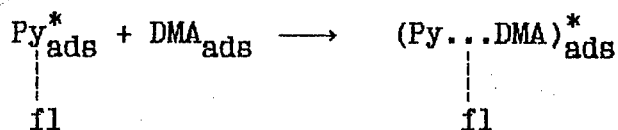
PHOTOINDUCED ELECTRON TRANSFER BETWEEN MOLECULES IN SILICA MATRICES

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The introduction of photoreactive molecules into a dispersed oxide composition is an attractive way to create light-transforming photosensitive systems with a wide set of unique spectral properties. Various promising applications of these novel materials include photochromic systems, lasers, light guides etc. Photoinduced electron transfer and charge separation in heterogeneous media such as silica is enhanced due to processes of adsorption and incorporation of host molecules. The photochemical reaction of exciplex formation between pyrene and dimethylaniline is often used as a model reaction for CT interaction in heterogeneous media such as micelles and polyelectrolytes. In the present report the same system is proposed for studies of adsorption and photoreaction on the nonporous silica surface - aerosil in the presence of non-ionic surfactant Triton X 100 micelles. Steady-state and dynamic fluorescence spectra and decay kinetics of luminescence of Py/DMA system in TX 100 micelles on aerosil A-300 $S_{sp} = 260 \text{ m}^2/\text{g}$ were investigated. The same processes on the A-300 surface during adsorption from hexane were studied in parallel. Under these conditions a reaction between Py and DMA runs in diffusion-controlled regime and fluorescence quenching of an Py^* adsorbate for the most part obeys Stern-Volmer equation.

An effect of the surface of a nonporous support on a course of a diffusion-controlled reaction



consist in a chemisorption of first portions of a quencher (0.1-0.4 % of a monolayer), a formation of a "quenching sphere" when coverages of a surface by amine approach to monolayer, a

concentration dependence of a quenching rate constant. Solubilisation of Py in TX 100 micelles gives 10 fold increase of its concentration on the surface and is not accompanied by Py_2 associates formation. Py fluorescence is quenched very strong by DMA adding in adsorbed on SiO_2 micelles of TX 100. When solubilized in the 2% solution TX 100, exciplex Py/DMA is formed for a higher DMA concentration then in hexane (a ratio of DMA/Py is 80:1 and 4:1, respectively).

Under conditions of a vacuum drying of Py/DMA/TX 100/ SiO_2 at the room temperature, a removal of an intermicellar liquid changes sharply photonics of the system. Luminescence of exciplexes disappears in the spectra and there are no Py quenching by DMA molecules. Addition of water to the system as well as excess of DMA molecules did not also influence the Py quenching onto SiO_2 surface. Intensity of Py fluorescence in these samples remained high and no quenching occurred. Irreversible structural and chemical transformations came in the system. It appears that coagulation of the pyrogenic silica in the TX 100 aqueous solution takes place with a formation of a colloidal sol when it being in the aqueous solution of TX 100, and on evacuation - a condensation accompanied by a change in the structure and dispersity (sol - gel - xerogel transformation). Hydrophobic Py molecules captured between layers of hydrophobic parts of TX 100 are encapsulated in the SiO_2 after drying and become inaccessible for quencher molecules.

PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF DYE MOLECULES IN POLYMERS USED FOR FLUORESCENT SOLAR CONCENTRATORS

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ABSTRACT

The photophysical and photochemical properties of the dyes have been extensively studied in the last decade, since these compounds have a lot of applications: dye lasers, solar energy conversion devices (including solar fluorescent concentrators), photosensitiser for chemical reaction and optical media for many applications.

The required features of all the dye molecules used for fluorescent solar concentrators are: high extinction coefficient, strong fluorescent properties, high quantum yields, and very good photostability.

Incorporation of the dyes in some polymer molecules could be one of the best methods for photostabilization of the studied dyes.

In this paper we present a spectroscopic study of some dyes (fluorescein, eosin, erythrosin, rhodamine B, rhodamine 6G, acridine orange) incorporated in different polymers (PEG 400, PEG 600, PEG 700), in order to establish the type of the interaction between the polymer and the dye, and the role of these interaction in the photodegradation reaction of the dyes.

These polymers were chosen on the basis of their capacity for formation of macromolecular complexes and hydrogen bonding ability, since these parameters are the most important in the energy transfer processes which can acts in the

photodegradation reaction of the dyes.

Absorption and emission spectroscopic techniques are applied in this study to elucidate the photophysical and photochemical properties of the studied dyes.

From the absorption and emission spectra of the dyes alone and in polymer solution, we can remark:

- a spectral shift of both absorption and fluorescence bands towards lower energy as the polymer-dye interaction becomes stronger. These blue shifts may be responsible for a stronger interaction (molecular complexes or hydrogen bonding formation) between the polymer and the dye;

- the fluorescence spectra of all the dye-polymer systems exhibit two different bands, one at lower energy (attributed to the dye) and the second at higher energy (attributed to the polymer).

The incorporation of the dyes in PEG 600 decrease the photodegradation rate of the studied dyes, much better than can do the other polymers (PEG 400 or PEG 700).

The use of these systems in fluorescent solar concentrators can lead to higher efficiency (89%) than the dyes alone (56%), the only explication being the photodegradation reaction of the dyes.

Fluorescence Lifetimes of Adsorbed Polymethines

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Polymethine dyes are used as colourants and as spectral sensitizer. Thiocarbocyanine and thiadicarbocyanine dyes were studied in solution and on inert surfaces (CaF_2 , SiO_2), using steady state and time resolved fluorescence spectroscopy. Fluorescence life times are strongly dependent on the environment. The deactivation processes of importance are nonradiative decay and fluorescence. The rate constant of fluorescence is independent from the environment. The widely accepted model for the S_1 deactivation of polymethines is torsion of the polymethine chain leading to an 90° configuration, with the very fast S_1 - S_0 deactivation, mostly reverting to the trans isomer in S_0 , but also forming a small amount of the cis isomer. In the adsorbed state, the quantum yield of fluorescence increases and shows a strong concentration dependence. For analytical applications the enhanced concentration dependence is very interesting. To investigate the reasons, we studied 3,3'-Diethylthiocarbocyanine iodide (DTCC) and 3,3'-Diethylthiadibocyanine chloride (DTDC) in different solvents and on CaF_2 (diameter appr. $16 \mu\text{m}$). The adsorption isotherms of DTCC and DTDC on CaF_2 are of non-Langmuir type. This means that the dye molecules are weakly adsorbed, no strong surface centres are involved and a sorptive interaction exists between them. Absorption and fluorescence spectra of solved and adsorbed dyes show only small differences, attributed to different refractive indices and restrictions in the adsorbed state for vibrational motions. The fluorescence life times ((time-resolved single-photon counting apparatus TR SPC 100 with mode-locked argon ion laser and dye lasers), using a monoexponential decay function are not constant and start to decrease even at surface concentrations which are much less than one monolayer. To explain the quenching observed at concentrations lower than those at which dimer formation can be experimentally detected, Förster energy transfer between the adsorbed molecules was tested. The formation of dimers was demonstrated by diffuse reflectance spectra, using the Kubelka-Munk function and transforming this values into $F(R_\infty)$ diagrams for spectral regions in which both, dimer and monomers absorb. Deviations from straight lines are taken as indications of dimer formation (begin by roughly one half of a monolayer). The dimers are strong quenchers of the fluorescence, but even for surface concentrations much lower than one monolayer, Förster energy transfer must be taken into account.

Heterosupramolecular Chemistry : An approach to modulating function in molecular devices.

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Abstract

Addressable supramolecular function offers the prospect of constructing molecular devices. The constituent supramolecular entities may be photo-, electro-, iono-, magneto-, thermo-, mechano- or chemoactive, depending on whether they process photons, electrons or ions, respond to magnetic fields or to heat, undergo changes in mechanical properties or perform a chemical reaction. However, despite many beautiful examples of recognition-directed self-organisation of supramolecular assemblies, progress toward realisation of practical molecular devices has been slow.

The reasons for the limited progress to date are linked to the requirements that must be met by practical devices: Firstly, that they function at a supramolecular level within the organised assembly; secondly, that the function of each constituent supermolecule in a given assembly can be modulated independently; thirdly, that the state of modulation of each supermolecule in a given assembly can be determined individually, and finally, that the resulting device meet speed, reliability and cost specifications. In practice problems encountered include the following: Firstly, the constituent supermolecular units do not act independently; secondly, attempts to modulate supramolecular function typically involve incorporation of sub-units within a supermolecule that respond to external stimuli, an approach which to date has produced relatively small effects; thirdly, substrates supporting an organised assembly that are capable of effecting stimulus of the above sub-units and providing information concerning their modulation state have proved difficult to identify; finally, techniques that permit individual addressing of the constituent supermolecules of the molecular device have not yet been realised. Currently, workers in many laboratories are attempting to solve the above problems using a range of approaches.

Regarding substrates supporting an organised assembly that are capable of effecting modulation of supramolecular function and providing information concerning the modulation state, recent work directed toward development of a heterosupramolecular chemistry appears to offer new opportunities ¹⁻³. Specifically, upon replacing a molecular component in a supermolecule by a condensed phase nanostructure, referred to as a heterocomponent, a heterosupermolecule is formed. By analogy, heterosupramolecular chemistry is distinguished from the chemistry of molecules adsorbed at the heterocomponent surface as follows : Firstly, the intrinsic properties of the heterocomponent and molecular components are only slightly perturbed within the heterosupermolecule; and secondly, the properties of the heterosupermolecule are not a simple superposition of the properties of the heterocomponent and molecular components. That is, there exists a heterosupramolecular function. Further extending the analogy, a heterosupermolecule composed of a heterocomponent and a molecular component is referred to as a heterodiyad, one composed of a heterocomponent and two molecular components as a heterotriad and so forth.

As for supermolecules, linking of the constituent components of the heterosupermolecule and self-organisation of the resultant heterosupermolecules may be recognition-directed. As is also the case for supermolecules, addressability is a consequence of organisation. Uniquely however, because one of the components of the assembled heterosupermolecules is a condensed phase nanostructure, self-

organisation yields an intrinsic substrate capable of effecting stimulus of the above sub-units and providing information concerning their modulation state. The realisation of this approach and implications for design of molecular devices are the subjects of this paper.

Specifically, we report results for a heterosupramolecule consisting of a TiO_2 nanocrystallite attached to a linked viologen-quinone unit ⁴. The associated heterosupramolecular function is photo-induced vectorial electron flow. For the corresponding organised heterosupramolecular assembly we demonstrate the following: that bandgap excitation of a semiconductor nanocrystallite results in light-induced vectorial electron flow; that electrochemical modulation of the bulk properties of the nanocrystalline semiconductor substrate modulates heterosupramolecular function; and that the state of the intrinsic substrate provides information about the modulation state of the constituent heterosupramolecules.

We will also report results for a heterosupramolecule consisting of a TiO_2 nanocrystallite attached to a linked $\text{Ru}(\text{bpy})_3$ -viologen unit ⁵. The associated heterosupramolecular function is photo-induced bi-vectorial electron flow. For the corresponding organised heterosupramolecular assembly we demonstrate the following: that 532 nm excitation of the ruthenium complex results in light-induced vectorial electron flow to either the viologen or the semiconductor heterocomponent depending on the potential applied to the intrinsic semiconductor substrate; that electrochemical modulation of the bulk properties of the nanocrystalline semiconductor substrate modulates heterosupramolecular function; and that the state of the intrinsic substrate provides information about the modulation state of the constituent heterosupramolecules.

Finally, some general implications of this work will be considered.

Recent Publications

- (1) Marguerettaz, X.; O'Neill, R.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1994**, *116*, 2628.
- (2) Marguerettaz, X.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1994**, *116*, 5017.
- (3) Marguerettaz, X.; Redmond, G.; Rao, S. N.; Fitzmaurice, D. *Proceedings of the 13th International Symposium on Optical Materials Technology for Energy Efficiency and Solar Energy Conversion* : Freiburg, April 1994, in press.
- (4) Marguerettaz, X.; Redmond, G.; Rao, S. N.; Fitzmaurice, D. *J. Am. Chem. Soc.* paper submitted.
- (5) Marguerettaz, X.; Doyle, H.; Rao, S. N.; Fitzmaurice, D. *J. Am. Chem. Soc.* paper in preparation.

Nuclear wavepacket study of unimolecular reactions in ultrashort pulsed lasers

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In recent years, considerable attention has been given to so-called femto-second chemistry developed by Zewail's group[1]. This femto-chemistry means searching reaction processes in real time. Theoretically, nuclear wavepackets are created by femto-second pulses. Its centroid corresponds to the classical representative point moving on the potential energy surface.

The purpose of this paper is two-fold. One is to clarify the mechanisms of unimolecular reactions induced by femto-second pulsed lasers in terms of the nuclear wavepacket propagation. We examined unimolecular reactions such as non-adiabatic reaction of sodium iodide[2], and photodissociation and hydrogen-migration of hydrogen cyanide[3]. The other is to present a theoretical work on controlling reaction dynamics by nonstationary lasers[4]. The theory is based on optimization of the laser field locally in time. The molecular system is expressed in the nuclear wavepacket representation. The theory was applied to laser-induced ring-puckering isomerization. The result indicated that nearly 100% of the population can be transferred to the final product state by irradiation of the optimized lasers.

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Metal Recognition and Photosensitizing Properties of Novel Squaraine Dyes

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Design of new fluoroionophores, which essentially consists of fluorophores linked to ionophores, is an active area of research due to their potential applications in the field of molecular information processing and in the sensing of low concentrations of biologically important cations such as Li^+ , Na^+ , K^+ and Ca^{2+} . For intracellular applications it would be necessary to synthesize fluoroionophores which have absorption and emission in the near infrared region and are soluble in aqueous systems.

Several squaraine dyes are known to have strong absorption and emission properties in the near-infrared region. Due to the intramolecular charge-transfer nature of these electronic transitions, which are highly sensitive to substitutional changes as well as the nature of the solvent medium, these dyes would be ideally suited for the design of new fluoroionophores. An additional property that these dyes possess is their ability to undergo reversible redox processes. Ionophores covalently linked to redox-active residues are very important as potential sensitive probes for metal ions as well as for transport of metal ions across membranes. Such dyes are also useful as photosensitizers in solar energy conversion.

Three new crown-ether linked squaraine fluoroionophores **1-3** have been synthesized and characterized (Chart 1). The ^{13}C NMR spectra of these dyes are indicative of their highly symmetric structure. The fluoroionophores **2** and **3** form aggregates in aqueous solution. Addition of β -cyclodextrin breaks up this aggregate leading to the formation of a fluorescent dye- β -CD complex. The fluoroionophore bearing N-aza-12-crown-4-ether (**1**) as well as N-aza-15-crown-5-ether (**2**) have a better selectivity for Li^+ ion and can be used as ion sensitive near-infrared probes. The synthesis, characterization of singlet and triplet excited states, redox properties as well as the metal binding properties of a new class of squaraine fluoroionophores **1-3** (Chart 1) will be presented.

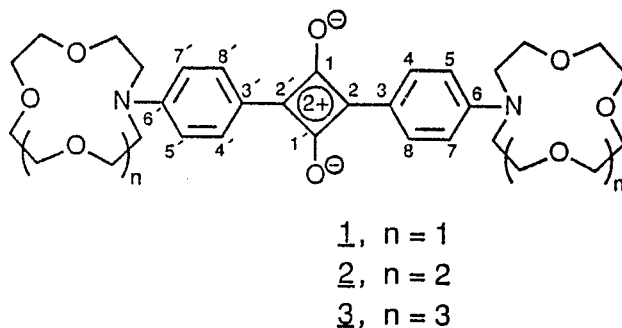


Chart 1

R2PI Detection and Spectroscopy of van der Waals Complexes of 4-Fluorostyrene with Rare Gases

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The spectroscopic study of van der Waals clusters in the gas phase offers the exciting prospect of bridging the gap between the gaseous and condensed phases by probing details of solvation at the molecular level. One of the most widely used spectroscopic method for investigating such interactions is multiphoton ionization combined with mass spectrometry. One color (1+1) resonance enhanced two photon ionization (R2PI) spectra of jet cooled 4-fluorostyrene van der Waals complexes with He, Ne, Ar, Kr and Xe will be reported. The measured spectra display discrete structure and allow the identification of electronic spectral shifts and stretching and bending frequencies of the various complexes. These spectra are discussed with the guidance of theoretical results. The minimum energy structures have been calculated starting from empirical atom-atom potentials. Calculated vibrational frequencies for these complexes agree well with the observed spectrum; the van der Waals bands can thus be assigned in detail. Different aggregation geometries are predicted in case of larger clusters.

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NANOCRYSTALLINE SOLAR CELLS. SCIENTIFIC PRINCIPLES AND ECONOMIC PERSPECTIVES

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Learning from the concepts used by green plants we have developed a molecular photovoltaic device whose overall efficiency for solar energy conversion to electricity presently attains 10%. The system is based on the charge transfer sensitization of nanocrystalline films. Similar to chlorophyll in the green leaf, the new photovoltaic device achieves very efficient light harvesting by a molecular absorber. The latter is grafted onto a nanocrystalline oxide semiconductor film of very high internal surface area. Photoinduced electron injection into the semiconductor generates electric charges which are collected by a conducting glass support. In analogy to photosynthesis this device achieves for the first time the separation of light absorption and charge carrier transport. Monochromatic incident photon to current conversion efficiencies approaching 100 % have been obtained. By virtue of its wide range of possible applications, its environmental compatibility, as well as the simplicity and low cost of production, the nanocrystalline solar cell should allow the exploitation of renewable energy and thus contribute to the achievement of sustainable development.

**Photolysis of Group 8 Metal Carbonyls:
Transient IR Spectroscopy, Photokinetics, and Quantum Yields of CO Substitution**

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Photolysis of metal carbonyls in the presence of potential reactants provides convenient access to a wide variety of substituted derivatives or catalytically active species,^{2,3} carbonyliron photochemistry being among the classic examples. Multiple CO photosubstitution is commonly observed upon continuous irradiation. Thus, $\text{Fe}(\text{CO})_5$ is readily converted into mixtures of $\text{Fe}(\text{CO})_{5-n}\text{L}_n$ photoproducts, with n depending on the nature of the incoming ligand L and on the reaction conditions.

Flash photolysis in combination with fast, time-resolved IR spectroscopy is the method of choice for the characterization of short-lived metal carbonyl intermediates involved in such processes, as it provides both kinetic and structural information. With a global as the IR monitoring light source, the instrumentation currently used in this laboratory⁴ has a system response time of 1–2 μs . This way, the $\text{Fe}(\text{CO})_4\cdot\text{solv}$ fragment is observed as a transient species generated upon laser flash excitation (308 nm, XeCl excimer laser) of the parent $\text{Fe}(\text{CO})_5$ in cyclohexane solution at ambient temperature. It shows a CO stretching vibrational band pattern indicative of a C_{2v} structure. In the absence of any potential ligand it decays within <20 μs with formation of $\text{Fe}_2(\text{CO})_9$. Trapping of $\text{Fe}(\text{CO})_4\cdot\text{solv}$ by a strongly binding donor ligand L , such as trimethyl phosphite, ultimately results in the formation of $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$, the ratio of which is governed by the concentration of L . Transient species assigned as $\text{Fe}(\text{CO})_3\text{L}\cdot\text{solv}$ (with a facial $\text{Fe}(\text{CO})_3$ skeleton) and $\text{Fe}_2(\text{CO})_8\text{L}$ are detected as intermediates en route to the final products.

The gradual conversion of $\text{Fe}(\text{CO})_5$ (up to 70–80 %) into the substituted $\text{Fe}(\text{CO})_{5-n}\text{L}_n$ products ($n = 1-3$; $L = \text{trimethyl phosphite}$) upon continuous irradiation at three different wavelengths (254, 302, and 365 nm) was monitored by means of quantitative IR spectroscopy, while light absorption was measured using an electronically integrating actinometer. The results are interpreted in terms of a reaction scheme involving both consecutive and direct formation of multiply substituted products. Quantum yields of the individual steps are evaluated on the basis of the appropriate photokinetic formalism, which accounts for mutual internal light filtering by all four complexes present in the reaction mixtures. Noteworthy, the predominant portion of $\text{Fe}(\text{CO})_5$ is directly converted into the disubstituted $\text{Fe}(\text{CO})_3\text{L}_2$ product. This finding, which is in accordance with related studies by other workers,⁵ is easily rationalized on

the basis of the above time-resolved IR spectroscopic observations.

Complementary investigations starting with $\text{Os}(\text{CO})_5$ and $\text{Ru}(\text{CO})_5$ reveal that these compounds undergo multiple CO photosubstitution in an exclusively stepwise manner, whereby in the ruthenium case a thermal process makes a significant contribution to the first step. The cyclohexane-solvated $\text{M}(\text{CO})_4$ fragments ($\text{M} = \text{Ru}, \text{Os}$), expected to be formed as the primary photoproducts, apparently are too short-lived for detection with our time-resolved IR spectroscopic instrumentation. Instead, the secondary products $\text{M}_2(\text{CO})_9$ or $\text{M}(\text{CO})_4\text{L}$, formed in the absence or presence of a ligand L, appear almost instantaneously, unless the $\text{M}(\text{CO})_4$ fragments are transiently trapped by a more strongly solvating additive such as benzene or acetone.

In summary, the disappearance quantum yields of the iron triad $\text{M}(\text{CO})_5$ complexes range from range from ca. 0.4 to 0.9, with moderate variations in going from $\text{M} = \text{Fe}$ to Ru and Os , but with a general decrease upon increasing the wavelength of excitation. However, with regard to the formation of multiply substituted products this comparative study reveals a distinctly different behaviour of $\text{Fe}(\text{CO})_5$ on the one hand and $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ on the other hand.

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MOLECULAR MECHANISM OF PHOTSENSITIZATION IN DNA

GUIDO DE GUIDI

DIP. DI SCIENZE CHIMICHE, FAC. DI FARMACIA, UNIVERSITADI

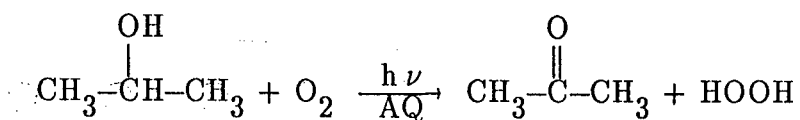
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SOLAR SYNTHESIS OF HYDROGEN PEROXIDE

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A series of novel solid catalysts have been developed which are capable of producing high yields of hydrogen peroxide when irradiated with sunlight in the presence of a suitable hydrogen donor, such as isopropanol. The overall stoichiometry of the reaction is



The reactions are carried out using a catalyst consisting of polymer-bound quinone groups chemically attached to solid hydrophilic surfaces such as silica gel, glass fibers or beads, and cellulose. Irradiation of solutions of the hydrogen donor in the presence of the solid catalyst with wavelengths of light absorbed by the quinone group while continuously introducing air or oxygen results in the oxidation of the alcohol to acetone and the simultaneous formation of hydrogen peroxide. The process can be carried out using either light from electrically driven lamps or natural sunlight. Operating the reaction in a sequential mode allows complete separation of the acetone and isopropanol from the aqueous solution of hydrogen peroxide. The catalyst is regenerated in the presence of air or oxygen and can be used for many cycles to produce oxidized organic molecules such as acetone, and hydrogen peroxide which is useful as a fuel, bleaching agent and chemical oxidant.

Characteristics of Si-a-As.Se.Cu solar cells.

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Chalcogenide Films and P-type Si junctions are rectifying at low fields and exhibit photodiode behaviour. The I-V characteristics of chalcogenide films and N-type Si junctions are similar to back-to-back schottky diodes.

The transport properties of the chalcogenide films are briefly reported and the cells performance are discussed.

Photochemotherapy with Cyanine Dyes

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The unique molecular architecture characteristic of cyanine dyes, and especially asymmetric merocyanine dyes, allows for selective recognition and uptake by leukemic cells. Since these dyes are highly fluorescent, this property provides for early diagnosis of leukemia in blood supplies. Furthermore, *in situ* photolysis of cyanine dyes can be used as a means for the specific destruction of infected cells, even in the presence of a high concentration of healthy cells. The mechanism whereby certain cyanine dyes recognize leukemic cells and facilitate their light-induced cytotoxicity will be discussed.

Understanding the mechanism for cellular destruction is exacerbated by the realization that the quantum yield for formation of the triplet excited state is extremely low ($\Phi_t < 0.005$) in most cases. This value can be increased substantially by incorporation of heteroatoms of relatively high atomic number (e.g., S or Se) into the molecular framework and triplet quantum yields up to 0.5 have been obtained in this way. The correlation between sensitization efficacy and triplet quantum yield provides for informative mechanistic insight. In addition to ineffective triplet state formation, these dyes undergo efficient *trans-cis* isomerization from the first excited singlet state and the resultant *cis*-isomer is highly photoactive. The rates of both photochemical (forward) and thermal (reverse) isomerizations depend weakly on the size of the rotor, as well as on the viscosity and polarity of the medium. Changing the nature and size of the dye also affects cellular uptake and internal distribution. The effects of these various parameters on the efficacy of cell photodestruction will be discussed.

PHOTOCHEMOTHERAPY ON EXPERIMENTAL BREAST TUMOR WITH PHOTOFRIN II AND LASER

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ABSTRACT

Therapeutic effects of photofrin II and argon ion laser on mice born sarcoma-180 tumor were investigated. S-180 cells (1×10^7) were implanted into the subcutaneous tissue of the breast part of ICR strain female mice. The tumor grew up to a volume of about $0.55 \pm 0.15 \text{ cm}^3$, the mice born tumor were divided into groups and treated with different doses of photofrin II (Pf II) and argon ion laser respectively.

The results showed sarcoma-180 cells were sensitive to Photofrin-II. The increased Photofrin-II dose resulted in increasing cytotoxicity compared to photosensitization following the small dose of photofrin-II. The best therapeutic effect (53.8% tumor control rate) was got in the group treated with 7.5 mg of Pf-II per kg of body weight and total irradiation energy of 75 J/cm² with 514.5 nm argon ion laser light. The most marked inhibitory effect of the survival rate of tumor cells was found in the group treated with Pf-II 7.5 mg/kg and laser irradiation 400 mW/4cm². The PDT groups inhibited DNA and RNA synthetic rate obviously , especially the group treated with 15 mg/kg of Pf-II and 400 mW of laser irradiation.

EXCITED STATE CHARACTERISTICS AND NEW UNACTIVATED C-H BOND
FUNCTIONALIZATION PHOTOCATALYSIS BY $W_{10}O_{32}^{4-}$

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The excited states of oxidatively robust and minimally toxic early transition metal oxygen anion clusters ("polyoxometalates" for convenience) cleave unactivated C-H bonds. The resulting radicals can be trapped by reduction, oxidation or other means, depending on the particular complex and conditions used, to form a range of products.¹⁻⁸

This versatile photochemistry has now been extended to include a catalytic method to carbonylate alkanes and a route to functionalize diamond surfaces. These new developments will be outlined.

New laser flash photolysis data in the picosecond and nanosecond time domains on the most useful and most studied polyoxometalate photocatalyst, $W_{10}O_{32}^{4-}$, indicate that a chemically active transient is formed after the very short lived and mildly emissive excited state.

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ELECTROLYTE AND TEMPERATURE EFFECTS IN PHOTOINDUCED INTERMOLECULAR ELECTRON-TRANSFER REACTIONS

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The bimolecular oxidative quenching of the metal-to-ligand charge-transfer excited state of $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) by methylviologen (N,N' -dimethyl-2,2'-bipyridinium cation; MV^{2+}) still serves, after twenty years, as the paradigm of electron-transfer quenching of excited $\text{Ru}(\text{II})$ -diimine complexes in fluid solution. Despite all the work that has been done on this system in aqueous solution, where it can effect the generation of H_2 , and, thus, the storage of solar energy, little is known about the specific effects of electrolyte ion-pairing on the rate constants of the quenching (k_q) and electron-transfer recombination (k_{rec}) reactions, and the cage escape yield (η_{ce}) of the redox products ($\text{Ru}(\text{bpy})_3^{3+}$ and $\text{MV}^{•+}$) into bulk solution. The research reported here was directed toward the identification of the molecular factors that affect these experimental parameters in order to optimize the efficiency of the overall energy storage.

Values of k_q , k_{rec} , and η_{ce} were determined as a function of the concentration of added salts, and, thus, ionic strength ($\mu = 0.01$ - 1.0 M) and temperature (10 - 60 °C). At 25 °C for Na^+ salts at constant [anion], k_q and k_{rec} increase in the order $\text{CH}_3\text{CO}_2^- \sim \text{H}_2\text{PO}_4^- < \text{HPO}_4^{2-} \sim \text{SO}_4^{2-} \ll \text{ClO}_4^-$; the trend in η_{ce} is in the opposite direction. For Cl^- salts, k_q and k_{rec} correlate to $[\text{Cl}^-]$, but not ionic strength, and are independent of the nature of the cation; η_{ce} decreases in the order $\text{La}^{3+} > \text{Ca}^{2+} \sim \text{Li}^+ > \text{Na}^+ > \text{Cs}^+$ at both constant μ and [cation]. For k_q and k_{rec} , activation energies are independent of concentration and the nature of the ions present (~ 16 kJ/mol), except in the case of ClO_4^- , for which E_a is $\sim 30\%$ lower. Similar effects are observed for η_{ce} .

Trends in k_q and k_{rec} are attributed to the existence of ion-paired aggregates of the cationic reactants and anions; correlations with the sizes, charges, and hydration enthalpies of the anions can be made. We suggest that ClO_4^- , with the smallest hydration radius and the least negative hydration enthalpy (being the least strongly hydrated of the anions studied), is more closely ion-paired within the $\text{Ru}(\text{bpy})_3^{2+}$ (or $\text{Ru}(\text{bpy})_3^{3+}$) interligand pockets, "tethering" the MV^{2+} (or $\text{MV}^{•+}$) into closer proximity, thereby lowering the activation barrier and increasing the rate of electron transfer. As a result, η_{ce} is also significantly lower for ClO_4^- . The dependence of η_{ce} on cation size suggest that the conventional model must be modified to account for reorientation of the geminate pair within the solvent cage.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

THE ROLE OF DOPANT DIPOLE MOMENTS ON CHARGE TRANSPORT BEHAVIOR IN MOLECULARLY DOPED POLYMERS

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Recently mechanisms of charge transfer in molecularly doped polymers are intensively investigated due to their wide application as photoreceptors in electrophotography. It was established that the mobilities of charge carriers in molecularly doped polymers are strongly dependent on the static dipole moment of the polar molecules. Dipolar disorder model has been invoked to explain these results[1]. In accordance with this model width of the density-of-hopping sites is determined by interaction of the localized carrier with molecule static dipole moment.

Accordingly to the proposed by us charge-carrier dipole traps model [2,3], electron-dipole interaction can cause charge-carriers trapping by dipole centers at low temperature in molecularly doped polymers as well. In this connection, one can directly observe by the methods of thermoactivated spectroscopy influence of dipole moments of guest molecules on a localized states in polymer, and also investigate processes of carrier detrapping and their dependence upon electric field, temperature and concentration of the polar molecules.

In this report we represent recent results of experimental study of localized states of charge carriers in poly-N-epoxy-propylcarbazole (PEPC) films doped with series of compounds with intermolecular charge transfer (CICT) molecules by thermo-luminescence (TL) and fractional glow technic. It should be stressed that among commonly used methods as TSC and time-of-flight measurements only TL is not influenced by the transport process and is directly related to detrapping. The large dipole moment of CICT molecules are mainly due to partial charge transfer in ground state between donor and acceptor parts of CICT. In such molecularly doped polymers we have detected appearance of dipole traps, whose depth is strongly dependent on the values of impurity dipole moments. Under condition of polar molecules concentration increase we have observed strong enhancement of trap activation energy and widening of local state density function.

Investigating electric field influence on termoluminescence, we have carried out direct measurements of dependence of dipole trap depth decrease with field augmentation both in strong fields and in very low fields. We have determined that for sufficiently strong field ($F > 5 \cdot 10^5$ V/cm) activation energy changes can be described by Poole-Frenkel (PF)-type expression: $dE_a(F) = C_1 \cdot F$, but constant C_1 smaller than PF-coefficient in several times. For low fields ($F < 5 \cdot 10^5$ V/cm) electric-field effect is differ from PF-law and can be described as $dE_a(F) = C_2 \cdot F^n$, where $n \approx 2/3$, C_2 -constant. These peculiarities of electric-field effect are compared with results of simulation of charge-carrier release from dipole traps in the presence of external electric field for molecularly doped polymers.

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**PHOTOCHEMISTRY AT HIGH TEMPERATURES: INTERACTION
OF ZnO WITH POSSIBLE PRODUCTS OF CO₂ REDUCTION**

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SWITZERLAND**

COMPARATIVE ELECTRON MICROSCOPY BETWEEN
HYPHAE FROM YOUNG AND OLD CULTURES OF
GAEUMANNOMYCES GRAMINIS V. TRITICI, THE
TAKE-ALL PATHOGEN OF WHEAT

By
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ABSTRACT

In hyphae in 4-8 day old cultures, the cell wall including the septum is mainly one layered. Normal cell organelles were observed except no dictyosomes (golgi apparatus). In hyphae in 30-day-old cultures, the cell wall is mainly two layered, with the outer one much denser than the internal, the septa is mainly trilayered, cell organelles, which had mostly deteriorated or showed sign of deterioration, are in most cases replaced by lipid granules; intrahyphal hyphae were observed growing within an old disintegrating one. The main storage material in young hyphae is glycogen, while in old hyphae are lipids.

EFFECT OF INFECTION WITH GAEUMANNOMYCES
GRAMINIS V. TRITICI ON WATER ECONOMY IN
WHEAT PLANT USING LEAD CHELATE METHOD

By

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ABSTRACT

Lead chelate solution, was used for the first time to study water economy in diseased wheat roots. The first primary root, of wheat seedlings, was marked and inoculated with agar strip method to obtain a well defined lesion on each root. The diseased plant absorbed much less, lead chelate solution, than healthy plant. The amount of lead sulphide in shoots of healthy plants was much higher than in the diseased plant. The amount of lead sulphide in the different parts of the infected roots particularly under the lesion were much higher than in the corresponding regions of the healthy root. After precipitation of lead, by exposing the plant to hydrogen disulphide, the shoots of healthy plants were greatly blackened. Meanwhile those of the infected plants showed no change in their colour or being slightly blackened. Microscopical examination revealed much lead sulphide accumulation in the diseased sections only. The method can be used with other plant pathogenic fungi, to study the pathway of water, in their hosts qualitatively and quantitatively.

FINE STRUCTURE OF THE PRIMARY ROOT OF

WHEAT INFECTED WITH GAEUMANNOMYCES

GRAMINS V. TRITICI

By

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ABSTRACT

Ultrathin sections were prepared, from healthy and diseased root tips and from the upper regions of the first primary root of wheat plant. Sections were stained in lead citrate and examined using electron microscope. The effect of fungal infections on the fine structure of the root was rather different in different parts of the root. In root tip cells no lignitubers were observed but a previously undescribed structure called a 'lignituber-like structure' was recorded in about 10% of the infected cells. Frequently the hyphae grew intercellularly. In the upper regions of the root the cell walls became more electron dense in advance of the developing hyphae, probably to lignification. Cell organelles also became electron dense at early stages of infection. Later both cell wall and cell contents disintegrated gradually, leaving remnants only. A fibrous structure and microtubules in bundles not previously recorded in the fungi but perhaps having a conductive role, ^{were} frequently observed in the hyphae in the upper regions of the root.

STUDY OF A Cu_2O BASED PHOTOELECTROCHEMICAL SOLAR CELLS.

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Abstracts :- A study of the photoelectrochemical response and stability of Cu_2O electrode is presented. This material is of interest because large amount of photo currents are generated for wavelengths $\lambda < 700$ nm. Some electrode deterioration occurs and this problem has been investigated as a function of bias voltage, by operation in non-aqueous solutions and by deposition of thin protective films.

Selforganization of chlorophylls in hydrocarbon solution and *in vivo* systems: Pico- and femtosecond relaxation in water bound Chla aggregates and *Cl.Tepidum* chlorosomes.

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Pico- and femtosecond absorption recovery measurements have been carried out for both *in vivo* and *in vitro* chlorophyll complexes. Three different types of Chlorophyll **a** (Chla) aggregates are formed in hydrocarbon solutions depending on the water content of the solution. Under very dry conditions a self-aggregate is formed showing a small red shift with respect to the chla monomer absorption. Adding water up to 5:1 ratio of water and Chla a 'dimer' absorption band at 702 nm is formed. When water Chla ratio is about 100:1 then an strongly red shifted chla water 'polymer' band is observed at 745 nm. Exciton splittings of several assumed aggregate structures were calculated and compared to the experimentally observed spectral shifts. Pico- and femtosecond studies of the shifted bands reveal further details of the aggregates. The picosecond rotation correlation time measurements suggest that the 702 nm band (lifetime of about 2.5 ns) originates from a Chla dimer. The femtosecond experiments of the 745 nm band suggest an extremely fast, about 0.5 ps relaxation of the S_1 state that accounts for some 75% of the signal. The 'polymer' aggregate involved is assumed to have a helical structure that may contain up a few hundred monomer units bound together by two water molecules. To get experimental insight to the decay mechanism we have performed the measurements in two solvents hexane and 3-methylpentane and at several temperatures. The decay kinetics seems to be non-exponential and we may only speculate at the moment on the origin of the relaxation process. Coherent effects and vibronic coupling to low-frequency modes may be involved. The low-frequency modes of the hydrogen bonding between the water and the Chla molecules of the aggregate may be involved in the relaxation process. Femtosecond results for the chlorosomes of *Chlorobium Tepidum* are very similar to what we obtain for Chla 'polymer' aggregates.

UNUSUALLY STRONG EMISSION FROM EXCIPLEXES FORMED BETWEEN BENZENOID SOLVENTS AND DIBENZOYLMETHANATOBORON FLUORIDE

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Singlet dibenzoylmethanatorboron difluoride (DBMBF) forms highly fluorescent exciplexes with benzene derivatives in the neat aromatic solvents. With the methyl substituted benzenes, the first process observed in acetonitrile solution is the quenching of the moderate fluorescence (*ca.* 0.1) of the short-lived (0.34 ns) DBMBF singlet excited state, before the exciplex emission becomes detectable when the aromatics concentrations is higher than 6M. In their own aromatic solvent, the fluorescence quantum yield of the exciplex is important (from 0.4 to 0.7). Its lifetime increases with the electron-donating properties of the aromatics, to reach about 23 ns for isodurene. When the exciplex becomes detectable (and this happens only when the polarity of the solvent mixture is small), its lifetime increases with the concentration of the aromatics as a result of the displacement toward the exciplex of its equilibrium with DBMBF. However, as the electron-donating property of the aromatics increases, the charge-transfer character of the exciplex increases also, and the collapse point of the exciplex comes at lower concentration of the aromatics.

In non polar solvents, such as cyclohexane, the situation is quite different, and the formation of the exciplex is observed immediately with the addition of the aromatics which quenches the emission of DBMBF (it fluoresces with a quantum yield of 0.046 and decays with a lifetime of 0.15 ns in pure cyclohexane). The quenching of DBMBF singlet excited state by the aromatics occurs with a rate constant greater than $10^9 \text{ M}^{-1} \text{ s}^{-1}$. As in acetonitrile for high aromatics concentrations, the singlet excited state of DBMBF is in equilibrium with the exciplex but now even at low aromatics concentrations. The equilibrium constant is *ca.* 5 with benzene and 25 with toluene. When the electron-donating property of the aromatics increases, the exciplex itself equilibrates with a triplex by interreaction with a second molecule of the aromatics. In the case of para-xylene, the only one that we could solve, the rate constant for exciplex formation is $1.7 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, that of the back reaction being $0.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ while the triplex is formed from the exciplex with a rate constant of $8 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$; the equilibrium between the two species is 0.6 thus favoring the formation of the exciplex entity.

The triplet excited state of DBMBF is formed in acetonitrile solution with a quantum yield of 0.01 and it has a 17.5 μs lifetime. This triplet is completely erased in the presence of a diene.

Structure and Properties of Nonplanar Porphyrins

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The diverse biological functions expressed by tetrapyrrole complexes of proteins such as chlorophyll reaction centre and antenna systems, heme proteins and cytochromes can directly be traced to nonplanar conformations of tetrapyrrole moieties. The different extents of distortion of the pyrrole rings of the porphyrin core is modulated by the nature and number of substituents, central metal ion, nature of axial ligands, charge of the porphyrin core, aggregation and packing effects in crystals. The synthesis of tetrapyrroles with varying degree of nonplanarity allows detailed studies using structural, spectroscopic and electrochemical redox methods. Three-dimensional structures of a few β -substituted dinitro and trinitro tetraphenylporphyrin, β -halo substituted tetraphenylporphyrin, mono-meso substituted octaalkyl porphines permit a range of distortions of the porphyrin. Detailed AMI calculations were performed on several of these systems using available structural data. The large shifts in the absorption bands of the porphyrin in the UV and visible regions and the dramatic shifts in the one-electron porphyrin ring reduction and oxidation potentials are caused by a complex interplay of the ruffling of the porphyrin core and the electronic effect introduced by the nature of the substituents. An analysis of these data will be presented with reference to their importance in chemical reactivities.

Mimicking Primary Processes of Photosynthesis - Model Compounds, Light-Induced Charge Separation -

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Photoredox processes in anisotropic media, such as vesicles, micelles and liquid crystals have attracted attention as mimicking electron transfer (ET) across biological membranes. In this paper we present photochemical investigations of covalently linked porphyrin quinones (P-Q's) in isotropic solutions, embedded in reversed micelles and in nematic phases of liquid crystals.

Reversed Micelles: Using steady state *in situ* lamp irradiation through resonator slits various P-Q's can be converted to paramagnetic derivatives. The species generated *via* intra- and intermolecular electron transfer (ET) processes can readily be identified as semiquinone radical anions and porphyrin cations of the P-Q's. Interestingly, depending on the experimental conditions, EPR spectra not only occur in absorption, rather, emissive signals can be observed, too. This finding is indicative of a strong electron spin polarization (ESP) mechanism.

The ESP effects yield valuable information about ET mechanisms and spin dynamics. The photoinduced reactions start, of course, with *intramolecular* ET from the singlet excited state of the porphyrin to the quinone moiety. This charge-separated state experiences ET back transfer to ground state or, alternatively, *intermolecular* ET to another P-Q molecule. Moreover, the quinone can be reduced to the hydroquinone redox state yielding P-QH₂. In this species, singlet ET from the excited porphyrin state can no longer occur and the triplet state is born *via* spin-orbit intersystem crossing. The polarization pattern observed under illumination in reversed micelles can be interpreted as arising from radical/triplet pair interactions.

Liquid Crystals: Time-resolved EPR studies performed on P-Q's in nematic phases of liquid crystals yield well-resolved, spin-polarized EPR spectra. Information of ET mechanisms in the anisotropic medium can be elucidated from the polarization pattern. Moreover, an interesting photoinduced conformational change, specifically back folding of the quinone moiety over the porphyrin, could be observed in the case of flexible spacers.

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Characterization of photosynthetic antennas by Nonlinear Polarization Spectroscopy (Frequency Domain)

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Indications of heterogeneity in the red/NIR absorption spectra of photosynthetic antennas are of interest with respect to their structural and functional differentiation and the role of possible "(B)Chl-forms" in efficient energy transfer. Up to now, there are only indirect indications of spectral substructures, at least at physiological temperatures.

We will report on a progress in this field, based on the application of nonlinear polarization spectroscopy in the frequency domain (NLPF) - a novel in photosynthesis research three wave mixing technique [1, 2]. The general content of information of NLPF includes

- i) the mode of absorption band broadening (homogeneous; extreme or moderate inhomogeneous; heterogeneous),
- ii) the ps/fs energy (T_1) and phase (T_2) relaxation and spectral diffusion (T_3) times,
- iii) the routes of energy transfer,
- iv) excitonic interactions and annihilation.

A special advantage of the NLPF method with respect to photobiological problems is their applicability at physiological temperatures.

Here we report on NLPF in the Chl a/b Q_y bands of trimeric and (Mg^{++} -induced) aggregated light-harvesting complex II (LHC II) of higher plant thylakoids [3]. For both samples, NLPF gives evidence of heterogeneous broadening with at least four subbands each. Their T_2 times are in the range of some 10 fs. Results on the above mentioned subjects ii) - iv) will also be discussed and compared to NLPF results with LH 2 antennas of purple bacteria [4].

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Fluorescence Spectroscopy of Polynuclear Aromatic Compounds (PAC) and Mineral Oils in Environmental Monitoring

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Due to the widespread occurrence and high carcinogenic potential of many PAC their analysis and quantification in environmental compartments is of prime importance. Laser spectroscopy has been established as an important tool in environmental research. Among the various spectroscopic techniques employed, laser-induced fluorescence is distinguished by outstanding sensitivity and high selectivity, and has therefore found considerable fundamental and practical interest. However, due to the heterogeneity and opacity of soil matrices, the qualitative and quantitative investigation of fluorescence signals obtained from soil-containing environmental compartments imposes usually considerable experimental difficulties.

In order to investigate the benefits and limitations of luminescence analysis in humic acid- and soil-containing samples we use selected PAC as model fluorophores and mineral oils as realistic contaminants. Single- and multi-channel stationary and time-resolved fluorescence measurements were performed to obtain basic photophysical information and experimental data relevant for the in-situ and on-line analysis of soil-containing samples. Results of the following investigations will be presented:

- Investigation of the quenching of PAC fluorescence by humic acids. The combination of stationary and time-resolved measurements provides insight in the mechanisms of fluorescence quenching and in fluorophore/humic acid-interactions.
- LIF-measurements directly from the surface of soils doped with model and mineral oils. Quantitative relationships between fluorescence intensities and concentrations were obtained in ranges relevant for realistic PAC and mineral oil contamination of soils.
- In-situ and on-line LIF-measurements on soil columns and in bioreactors. The determination of probability distributions of fluorescence signal intensities yield information about the distribution of the contaminants on the soil surface and the degree of heterogeneity in these systems.

The results obtained in these studies will be evaluated with regard to the development and application of in-situ and on-line luminescence analytical methods under conditions realistic e. g. for soil decontamination processing.

A Non-Silver Dry-Processed Photographic Arts Film

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Abstract

A new non-silver dry-processed electrophotographic imaging film based on particle migration imaging technologies will be described. The new film contains a monolayer of submicron-sized (0.35 microns) selenium particles embedded in a polymer matrix. Film processing involves brief heating of the film which reduces the viscosity of the polymer matrix to allow the photo-exposed charged selenium particles to migrate in depth to yield a high resolution optical image. The imaging material offer high-resolution, laser-sensitivity in either the blue-green or red to infra-red, fast dry processing without any effluent, room-light handling, excellent shelf life and image stability. By eliminating the wet chemical processing of conventional silver films, the new materials provide an environmentally friendly alternative for many graphic arts applications. In this presentation the materials, the imaging processes, the imaging properties as well as their plate-making and printing characteristics will be described.

INTEGRATED TECHNOLOGY FOR DESERT FARMING WITH SOIL CONDITIONER "RAPG"

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The aridity of deserts is argued to lack of water, nature of soils and meteorological factors. Nowadays the irrigation technology makes the underground water available. Soil conditioner "RAPG" changes desert soil into arable land. It grows successfully different vegetables, crops, fodder's, trees, shrubs and ornamental plants.

Yet, excessive solar radiation reduces efficiency of the photosynthesis and enhances respiration and transpiration. The scorching heat at the long summer dries soils and suppresses biological activity in the rhizosphere. Thus, the productivity is essentially lowered.

To integrate our technology for desert farming, we contrived canopies perennial trees. A long three consecutive years, canopies of peanut (*Arachis, hypogaea, L.*), roselle (*Hibiscus sabdariffa, L.,*) and sunflower (*Helianthus annuus, L.*) as well as others have been investigated. Although three crops are gained per unit area within the season the productivity of each one has increased by 10-15% as compared with being alone in the same area.

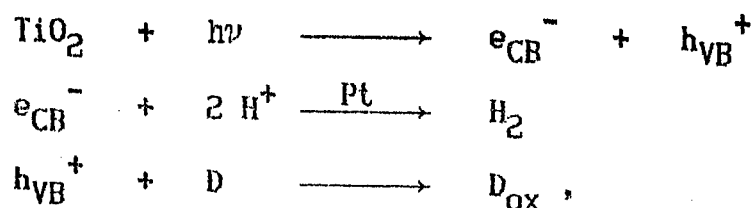
This is besides evident conservation of moisture and buildup efficacious biological fertility. Detailed technology is described. It is highly economic and renders farming of desert greatly profitable.

MECHANISM OF PHOTOCATALYTIC HYDROGEN PRODUCTION IN THE Pt/TiO₂/OXALIC ACID SYSTEM

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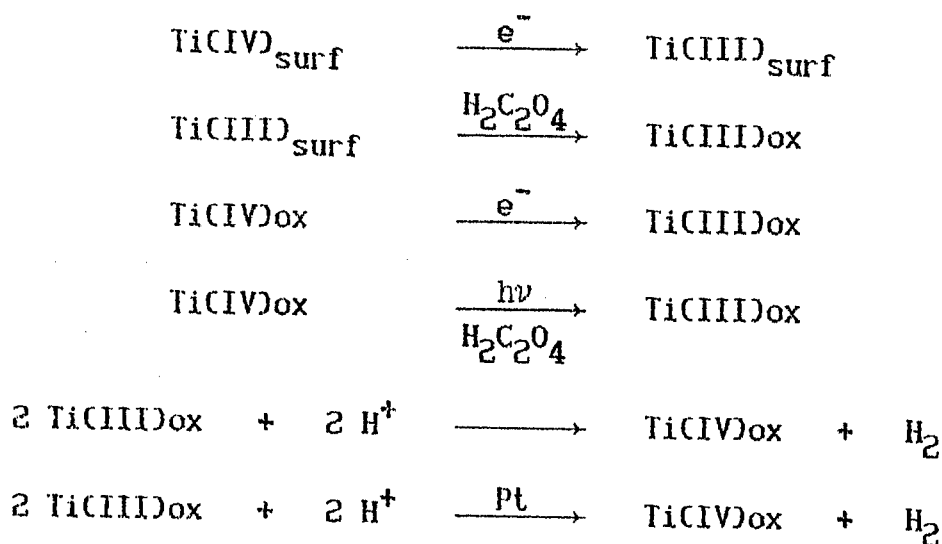
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Hydrogen evolution from the aqueous Pt/TiO₂ suspensions in the presence of an electron donor D is described by the scheme:



where e_{CB}^- is a conduction band electron and h_{VB}^+ is valence band hole.

We found that the photo-induced dissolution of TiO₂ in the presence of oxalic acid as donor changes above mechanism [1]. Titanium (III) oxalate Ti(III)ox (the product of the dissolution) takes part in hydrogen evolution:



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PHOTO-INDUCED OXIDATION OF PYROCATECHOL
OVER TITANIUM DIOXIDE

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The photocatalytic degradation of organic pollutants over the semiconductors is a promising method for water purification. The most active and stable semiconductor for this purpose is titanium dioxide. Some pollutants or the intermediate products of their photooxidation can form the charge transfer surface complexes CTSC with the surface titanium ions of the TiO_2 particles. CTSC of salicylic acid on TiO_2 changes the kinetics of the ligand photooxidation [1]. Recently we have found that the CTSC with some ligands - electron donors effect on photocatalytic hydrogen production from the aqueous Pt/TiO_2 dispersions [2].

Here we studied the photo-induced transformation of pyrocatechol PC over TiO_2 . The titanium ions is known to form with PC brown colored the charge transfer complex in aqueous solutions. The TiO_2 surface is became yellow brown at addition of PC to the aqueous TiO_2 suspension owing to the CTSC formation on TiO_2 . The diffuse reflectance spectrum of dry TiO_2 powder with chemisorbed pyrocatechol PC/ TiO_2 exhibits a broad band in the visible.

Irradiation of aqueous PC/ TiO_2 suspension by light of xenon lamp changes the color of the semiconductor surface to dark brown or black brown. This product of the photo-induced transformation of PC was attributed to phenolic oligomers "artificial humic acids".

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PHOTOCHROMIC MATERIALS: A COMPREHENSIVE KINETIC, THERMODYNAMIC AND PHOTOCHEMICAL STUDY

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Photochromism, that is the photoinduced reversible transformation of a chemical species into another one having a different absorption spectrum, has raised great interest over the last decade because of the multiplicity of actual or potential applications.

In this work, some spiroindoline-oxazine (SO, colourless) \leftrightarrow photomerocyanine (PM, coloured) systems have been investigated with the aim to answer several questions:

- Which is the colour of PM and how is it influenced by structural and environmental factors ?
- How important is thermochromism and how is it affected by the solvent and structure ?
- How fast is the thermal bleaching and how much is it temperature dependent ?
- Is it possible to give a quantitative evaluation of "colourability" under pulsed or steady state irradiation ?
- How can the sensitivity of these materials be shifted towards the solar spectrum ?
- Which is the durability of these systems ?

Answering these questions means a complete understanding of the photochromic properties of these molecules. This required to determine solvent spectral shifts of the PM colour absorption band (solvatochromism), to measure thermodynamic (equilibrium constant, enthalpy, entropy) and kinetic (rate coefficient, activation energy, frequency factor) parameters of the reaction, to evaluate the PM molar absorption coefficient and the photoreaction quantum yield, to investigate the possibility to photosensitize the reaction utilizing lower energy light and to study the mechanisms of the photodegradative processes.

The results obtained give an overall picture of the physico-chemical and photophysical properties of these systems and help to find criteria to test them with respect to potential applications.

PHOTORADICAL AGEING OF SOLID POLYMERS

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In this communications concerning different carbon-chain and hetero-chain polymers we would like not only provide information on the basic mechanisms of reactions of electronically excited radicals and radical anions but to show how these processes can affect the molecular weight and functional composition of polymers.

New data referring to the mechanism and quantum efficiency of electronically excited macroradicals and radical anions reactions in various carbon- and hetero-chain polymers at temperature below glass transition or melting points are presented and discussed. Basic mechanisms of radicals photochemical reactions, including new data on the mechanism of photochemical reactions of peroxide, allyl, polymethyl methacrylate end macroradicals, obtained with the use of matrix isolation on the activated silica surface method, the effect of various factors (photon energy, free volume, molecular organization of the medium, including different degree of crystallinity) on the direction and efficiency of electronically excited macroradicals reactions are considered.

The important role of photochemical chain reactions in photoageing, including photooxidation of polymers (polystyrene) is demonstrated. Data concerning photoradical chain length in different polymers, their dependence on the photolysis time are presented. Based on the method of statistical testing, such parameters of the photoradical chain reaction as the chain length, distance of the elementary migration of the radical centre, recombination radius of radicals are determined.

It was found that by varying photon energy, temperature, photolysis time and taking advantage of competition between thermal and photochemical reactions, it is possible to change the functional composition and molecular weight distribution of polymers.

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PHOTOINDUCED INTRAMOLECULAR CHARGE SEPARATION IN MIXED LIGAND
DITHIOLATO - α,α' -DIIMINE ZINC COMPLEXES

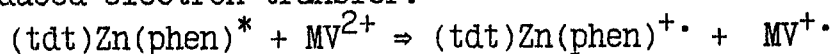
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Emission properties in the series of complexes $(4-X-C_6H_4S)_2Zn(phen)$ in frozen solutions were found to be drastically dependent on the nature of para-substituent in the phenylthiolate ligand [1]. The emission from the both phenanthroline localized intraligand (IL) and charge separated ligand to ligand (LLCT) triplet states was observed for $X = H, Me$ and tBu substituted complexes, methoxy-substituted one emits only from LLCT state and Me_2N - substituted complex is not luminescent. The both emitting states were shown to be populated from the lowest LLCT singlet excited state as they have the same excitation spectra within LLCT absorption region. The lifetimes of upper lying IL states are of 0.2 s order and don't depend on substituent nature or temperature indicating the absence of thermally activated radiationless decay processes involving the coupling with lower lying LLCT states. The IL state population quantum yields estimated by ESR technique at 77 K were found to be 0.6 and 0.07 for H- and alkyl-substituted complexes independently on alkyl group volume. They are decreased with temperature and 9.2 and 6.7 kJ/mol activation energies assigned to thermally activated nonradiative relaxation processes in LLCT singlet states have been measured. Nonradiative relaxation in triplet LLCT states also was found to be thermally activated with a tendency to lowering the corresponding activation energies from 14.2 kJ/mol ($X=H$) to 1.8 kJ/mol ($X=MeO$) along with the growth of p-substituent electron donating ability.

It was shown that the dithiolate-diimine zinc complexes with 3,4-toluenedithiolate (tdt) donor ligands: $(tdt)Zn(bpy)$, $(tdt)Zn(phen)$, $(tdt)Zn(biqu)$ have no luminescence nor in the liquid solution at 298 K neither in the glassy solution at 77 K because LLCT transition is lowest in energy and symmetry forbidden.

LLCT states in solution are subjected to dissociation on arylthiyl radical and reduced zinc-phenantroline moiety as it was stated by using of flash photolysis and ESR spin trapping techniques [2]. Such a process is considered to be responsible for thermally dependent nonradiative decay channels in frozen solutions. Two models were involved to explain an unusual dual luminescent properties of some complexes in solid solutions: one taking into account possible structural nonequivalence leading to variances in excited states order of emitting species, and the other based on a considerable difference in IL and relaxed LLCT triplet states geometries leading to high activation energies for intramolecular electron transfer. In the frames of both models substituent effects may be connected with the possibility of interligand three-electron bonding between thiolate ligands stabilizing LLCT states towards dissociation.

It has been found experimentally that excitation of complexes with tdt donor ligands in the presence of methyl viologen (MV^{2+}) in degassed dimethylformamide solution leads to the photoinduced electron transfer:



Flash photolysis experiments intimate that decay of $MV^{\bullet+}$ after the flash is uncomplete. We assumed that back electron transfer compete with the irreversible decay on the oxydized form of the complex. The solution of the corresponding equations written under assumption that both reactions are bimolecular and diffusionally controlled with the equal rate konstants k gives: $Q + \ln(1 - Q) = k [MV^{\bullet+}]_0 t + \text{const.}$, $Q = [MV^{\bullet+}]_0 / [MV^{\bullet+}]$. Experimental data depicted in the coordinates $Q + \ln(1 - Q)$ vs t lay on the straight line rather well.

Authors thank Russian Foundation of Basic Research, project 93-03-5916, for financial support.

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Pulsed laser Ablation: Thin Film Production and Coating, Process Diagnostics

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Abstract

Pulsed laser deposition (PLD) has been largely applied for the fabrication of thin film deposits of a variety of materials. This technique has been used successfully to prepare dielectric, semiconductor and high temperature superconducting thin films. Various stages characterize the process of film preparation by laser ablation [1]. The process starts with coupling of the high flux of the laser electromagnetic radiation into the solid surface and ends with particles (vapor species) release and deposition. The initial mechanisms describing the laser-solid interaction may be defined basically as thermal or electronic, depending to a large extent on the laser fluence. Other sub-categories are also reported in the literature. Secondary mechanisms include all processes dealing with transport of the material ejected from the target [1,2]. Information gained from the measurement of the gasdynamics of the plasma plume travelling to the substrate will certainly improve the ability to produce quality thin films. The study of the formation and composition of the plume by means of in situ optical techniques and molecular beam mass spectrometry is relevant to this purpose.

The pulsed laser produced plasma plumes from AlN targets have been studied by spatially and temporally resolved optical spectroscopy, fast intensified CCD imaging and quadrupole. These techniques were used to monitor plume species gas dynamics during pulsed laser deposition of AlN and thin film preparation. The species formed by laser ablation in vacuum have also been measured by molecular beam mass spectrometry of the expanded plume.

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PHOTOLYSIS OF TRIAZENE-1-OXIDES¹⁾

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Photolysis of the 1,3-dipolar triazene-1-oxides 1a-d using
a 125-Watt high pressure mercury lamp in different solvents,
cyclohexane, ethanol and benzene led to their decomposition.

In cyclohexane, irradiation of 1a-d afforded 2-
hydroxyazobenzene 2 (7.3-10%) as well as the biaryls 3a-d (14.8-
17.9%) (see Fig. 1). However, their photolysis in benzene gave
beside 2-hydroxyazobenzene 2 (11.7-14.6%) and biaryls 3a-d, the
biaryls 4a-d (53.1- 58%) as major product. On the other hand, 2-
hydroxyazobenzene 2 (72.5-84.6%) and the arenes 5a-d were
produced from irradiation of 1a-d in ethanol.

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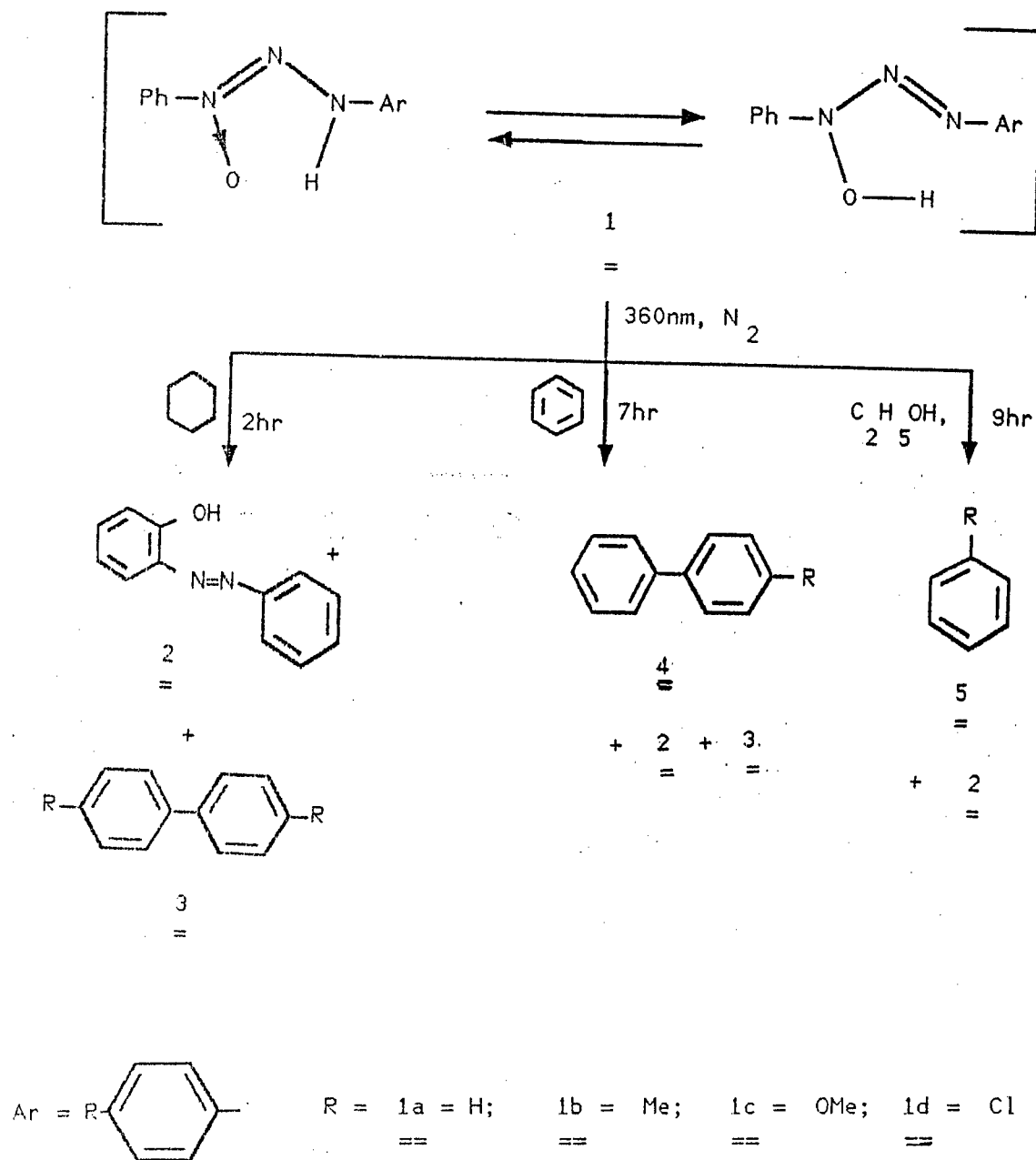


Fig. 1

**THE DYNAMICS OF EXCITONS IN THE J-AGGREGATES OF A
CARBOCYANINE DYE**

J. MOLL

BAM, RUDOWER CHAUSEE 5, HAUS 8.15

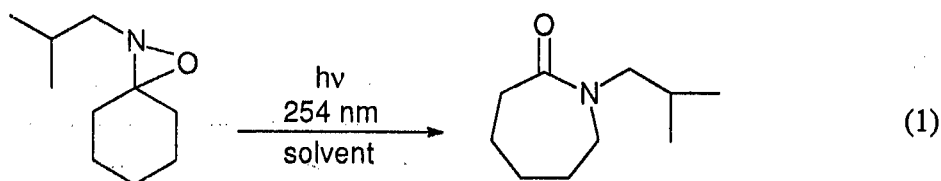
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PHOTOLYTIC REARRANGEMENTS OF OXAZIRIDINES

Alan J. Post and Harry Morrison

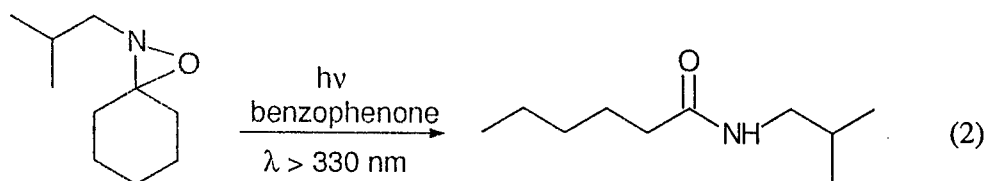
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2-Isobutyl-1,2-oxazaspiro[2.5]octane has been photolyzed in the presence of several aromatic potential sensitizers (anisole, toluene, N,N-dimethylaniline, benzonitrile) in hexane and acetonitrile using 254 nm light. All four aromatics sensitize rearrangement of the oxaziridine to a lactam (eqn 1), with rate constants for sensitization in the range of 0.1 to $2 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$. There is no obvious dependence of the rate constants on sensitizer ionization potential or solvent polarity. Quenching studies indicate that this is a singlet derived process, as seen by a shortening



of the toluene singlet lifetime in the presence of the title compound. The endothermic energetics for such energy transfer requires the involvement of a "nonvertical" process.

Triplet sensitization of the oxaziridine using benzophenone in hexane gives the open chain amide as the primary photoproduct (eqn 2). Using triplet sensitizers in which the lowest lying triplet state is switched from n, π^* to π, π^* indicates that a "biradical" n, π^* state is required for



this rearrangement to occur. Refluxing the oxaziridine in the presence of a radical initiator in isopropanol (generating the dimethylhydroxycarbonyl radical) also gives the amide. The use of solvents other than isopropanol results in no loss of the oxaziridine. From this evidence it is clear that triplet energy transfer is not the mechanism for the formation of amide, but rather a chemical sensitization occurring in the ground state.

In addition, we will present results of a study of a steroid containing a light harvesting chromophore at the 3 position and an oxaziridine at the 17 position.

Photochemical Synthesis of Tetrabridged Cyclophane

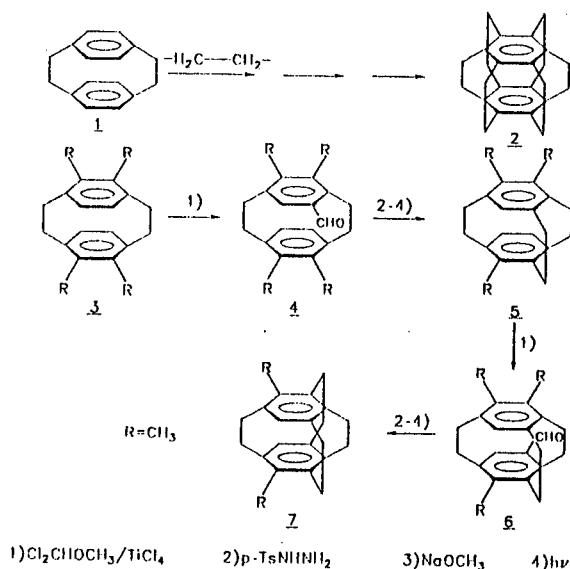
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Since the discovery of the parent cyclophane **1** in 1949¹, the synthesis of multibridged cyclophanes has attracted attention of many investigators. With the synthesis of [2₆](1,2,3,4,5,6) cyclophane^{2,3} (**2**, superphane) all of the possible isomers of the [2_n] series of cyclophanes are known.

The present study describes the synthesis of tetrabridged cyclophane **7** by transformation of **3** into the corresponding aldehydes followed by condensation with p-toluenesulfonyl hydrazide then irradiation with 500 W Vitalux lamp. Construction of the ethano-bridges has been achieved via carbene-insertion reaction.



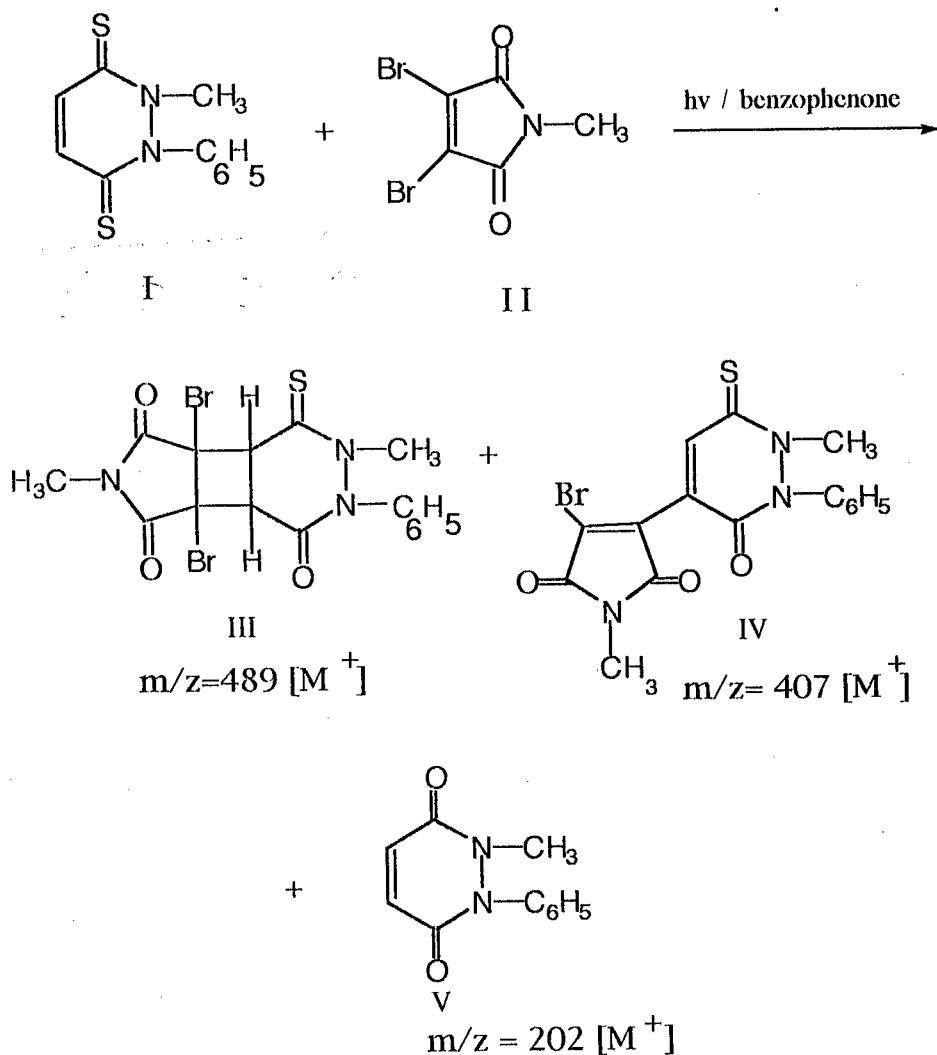
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THE PHOTOCHEMICAL REACTION OF DIBROMO-N-METHYLMALCIMIDE WITH 1-PHENYL-2-METHYL-1,2-DIHYDRO-3,6-PYRIDAZINEDITHIONE

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Irradiation of a mixture of 1-phenyl-2-methyl-1,2-dihydro-3,6-pyridazinedithione (I), dibromo-N-methylmaleimide (II), 10 mg of benzophenone, and acetone in a pyrex vessel ($\lambda > 313 \text{ nm}$) for 30 hrs using a high pressure Hg lamp (Philips HPK 125 W) afforded III, IV and V which were identified by analytical and spectroscopic tools. The $^1\text{H-NMR}$ spectrum of compound III reveals the presence of two doublets centered at $\delta = 3.65$ and $\delta = 3.85 \text{ ppm}$ due to the two hydrogen protons. Compound III which has a cyclobutane ring is expected to be formed by a mechanism including $[\pi^2_s + \pi^2_s \rightarrow 4]^\pm$.



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PHOTOELECTROCHEMICAL BEHAVIOR OF COUPLED SnO_2/CdSe SEMICONDUCTOR FILMS

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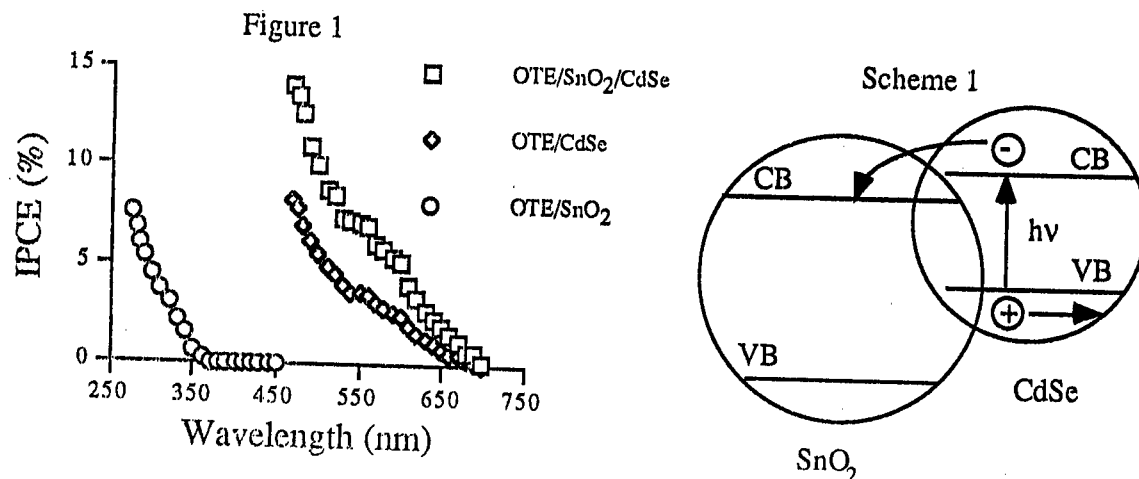
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In recent years, considerable interest has been shown in the synthesis of thin semiconductor films by electrochemical and chemical deposition as well as direct deposition of colloidal semiconductors ^{1,2,3} for the conversion of solar energy into electricity and chemical energy. However, one of the major problems in utilizing these thin semiconductor films in photoelectrochemical cells is the absence of a space charge layer at the semiconductor-electrolyte interface. Under these circumstances, photogenerated charge carriers can travel in both directions and can lead to the recombination of photogenerated electrons with holes instead of flowing in the external circuit. An interesting approach in achieving efficient charge separation in a semiconductor particulate system involves coupling two semiconductor particles with suitable energy levels^{1,4}. We have utilized this concept to develop coupled SnO_2/CdSe semiconductor films and have studied their photoelectrochemical behavior.

The nanocrystalline SnO_2 thin film electrodes have been prepared by coating the conducting surfaces of optically transparent electrodes (OTE) with colloidal SnO_2 semiconductor particles² (diameter 3nm). The thin CdSe films were electrochemically deposited onto bare OTE and SnO_2 -colloid-deposited OTE (OTE/SnO_2) electrodes using a SeO_2 -based bath³.

The incident photon-photocurrent efficiency (IPCE) of OTE/SnO_2 , OTE/CdSe and $\text{OTE}/\text{SnO}_2/\text{CdSe}$ electrodes are plotted in the figure 1. Since SnO_2 is a large bandgap semiconductor ($E_g = 3.8 \text{ eV}$), it can only be excited with the UV light. When coupled with CdSe, its photoresponse extends into the visible (up to 700 nm). Moreover, the results from this figure show that the coupling, indeed, increases the charge separation (IPCE increases from 9% for OTE/CdSe to 15 % for $\text{OTE}/\text{SnO}_2/\text{CdSe}$). The principle of charge separation in such a system is shown in Scheme 1. Upon optical excitation of CdSe, the photogenerated electrons are quickly transferred from excited CdSe ($E_{CB} = -1.00 \text{ V}$ vs

NHE) to the lower-lying conduction band of a SnO_2 ($E_{\text{CB}} = 0 \text{ V vs NHE}$) and thence to the external circuit.



Further evidence of the effect of the coupling is obtained from the cyclic voltammetry of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in the dark. It is seen that both OTE and OTE/CdSe electrodes exhibit reversible cyclic voltammetry peaks corresponding to the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ and reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ and hence indicating a free flow of electrons in both directions. However, OTE/SnO₂/CdSe electrode behaves differently with no characteristic redox peaks. These results suggest that the coupling of SnO₂ results in the suppression of electron flow toward the electrolyte. The photoelectrochemical performance utilizing OTE/SnO₂/CdSe electrode has also been evaluated and net conversion efficiency of 2 % has been obtained. Efforts are being made to sensitize these coupled systems with chlorophyll and other pigments.

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Acknowledgments:

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LOW FREQUENCY CAPACITANCE MEASUREMENTS OF ALUMINUM/MICROCRYSTALLINE CHLOROPHYLL a/SILVER SANDWICH CELLS

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The capacitance measurements of aluminum/microcrystalline chlorophyll a/silver sandwich cells have been carried out at various frequencies in the dark and under illumination using low frequency oscillographic technique. The results in dark show that the capacitance, C , is practically independent of the applied voltage, V , at frequencies higher than 10 Hz. However, as the frequency decreases, the capacitance begins to show dependence on the voltage, and a behavior characteristic of Schottky depletion layer, i.e. a linear $1/C^2$ vs V plot, can be seen at 0.1 Hz. The reason for this is the fact that the charges responsible for the depletion layer are mainly trapped charges. It should be mentioned that in the fabrication of Chl a cells, Chl a employed is in microcrystalline and not in monocrystalline form. It is thus possible that there are present a large number of structural imperfections that act as traps thus immobilizing the charges temporarily or permanently. So, when the capacitance measurements are made at higher frequencies, the charges responsible for the depletion layer are not able to follow the rapid variations in the applied voltage. Consequently, only the voltage-independent geometric capacitance (Chl a behaving as a dielectric) is observed. However, when the frequency is decreased and falls within the response time of trapped charges, the voltage-dependent capacitance begins to appear.

While the capacitance is voltage-dependent in dark at 1 Hz, the linear $1/C^2$ vs V plot is not observed; however, illumination with monochromatic light of adequate intensity yields a linear $1/C^2$ vs V plot characteristic of a Schottky

depletion layer. Although, the exact mechanism by which light is able to bring the response time of the trapped charges within the time variation of the applied voltage is not well understood, it is possible that the light supplies the necessary energy to detrapp the charges. The free charges are then able to respond to the variation in the applied voltage, and the capacitance measured is that of the Schottky depletion layer. It should be remarked that when the frequency of applied voltage is low, the intensity of the light required to obtain a linear $1/C^2$ vs V plot is also low. This is due to the fact that at low frequencies, a large number of charges are already able to follow the changes in applied voltage, and, thus, only a little amount of light is needed to mobilize the remainder of the charges. However, when the frequency is high, a large fraction of the charges fails to respond, and, as a result, relatively intense light is needed to mobilize the greater number of trapped charges.

The ageing of the cell in ambient air has been found to have dramatic effect on the capacitance characteristics of the cells. The diffusion of oxygen and the presence of water vapor are most probably responsible for an inhomogenous space charge developing within the depletion layer with time.

Acknowledgments:

This work has been supported by the Natural Sciences and Engineering Research Council of Canada. One of us (C.N) is grateful to Ministère de l'Éducation Nationale du Maroc for a fellowship.

PHOTODEGRADATION OF BUTYLTIN COMPOUNDS IN WATER: ENVIRONMENTAL IMPLICATIONS

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ABSTRACT: Tin has a larger number of its organometallic derivatives in commercial use than any other elements. Particularly, tributyltin (TBT) compounds, have come to have widely used as wood preservatives and antifouling paints, i.e. in preventing the attachment of water organism in immersed structures in sea water and fishpond factories.

Although inorganic tin compounds are basically not harmful, some organotin species are very toxic to both animal and vegetable life. Thus, very low levels of TBT, about $1 \mu\text{g L}^{-1}$, are lethal or causes reduced growth and reproduction of commercial shellfish. Since a few years, increasing concern has arisen about the impact of TBT and its degradation products in the aquatic environment. This concern has resulted in several studies of the photodegradation of TBT in natural sunlight on the surface of waters and sediments.

Although studies have proved the positive effect of UV-illumination on environmental degradation of butyltin compounds, however this process has its limitations. The maximum absorption wavelength of butyltin compounds are within the UV region 190-290 nm. Consequently, TBT species are degraded very slowly by natural sunlight. Moreover, the UV-photodegradation of TBT leads to the formation of partially oxidized products from the organic groups attached to the tin atoms. Accordingly, new methods must be developed. Heterogeneous photocatalysis has shown to be an attractive process for the degradation of many pollutants. Powdered titanium dioxide, TiO_2 , is one of the most promising photocatalyst for the detoxification of organic or inorganic contaminants in the aquatic environment.

This lecture will be concentrated on a comprehensive account of the fate of butyltin's photodegradation in environmental water by both UV-photolytic and TiO_2 -photocatalytic processes.

Femtosecond kinetics of chlorophyll a aggregates and chlorosomes.

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We describe one-color femtosecond pump and probe experiments performed around 750 nm for Chla-water aggregates in 3-methylpentane and in hexane solutions as well as for *Clorobium Tepidum* chlorosomes. We have used an amplified Ti:sapphire fs-laser, which operates at 1 kHz repetition rate. Also frequency-doubled Soret band excitation and fundamental probing was used to study the above systems. The observed kinetics shows a very fast non-exponential initial component of about 500 fs for all samples studied. The origin of this relaxation process is presently not understood. Solvent effects, coherent effects and coupling to low frequency hydrogen bonding modes may be involved. We have put some effort in trying to get reliable kinetic constants on the above fast kinetics. If too many exponential components to fit the signal are needed the outcome of the fitting procedure may strongly depend on the initial guess parameters. The errors of the each individual decay time and of the amplitudes may become large. We have used two different convolution programs to evaluate kinetic constants from the observed and apparently multiexponential decay signals. One is a commercial Global Analysis program package and the other is our own statistical multiexponential (from 200 to 1000 components) program. The rising part of the signal was symmetrized and used as an instrumental function. The results obtained by using the two convolution methods will be discussed.

**NOVEL VACUUM-UV- (VUV) AND UV-EXCIMER FLOW THROUGH
PHOTOREACTORS FOR WASTE WATER TREATMENT AND FOR
WAVELENGTHS SELECTIVE PHOTOCHEMISTRY**

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Incoherent VUV/UV-excimer sources [1] can be designed as flow through photoreactors [2] with positive geometry of radiation. The typical setup of a VUV/UV-excimer flow through photoreactor consists of a cylindrical quartz tube which is surrounded by a hermetically sealed annular discharge gap containing the excimer gas or gas mixture. Excimer formation and subsequent VUV/UV-emission is driven by a high frequency/high voltage plasma generator which is connected to electrodes located at the outer walls of the discharge gap. By applying an outer UV-reflecting electrode an inward directed radiation geometry is realized. The coupling of different excimer light sources to irradiation modules is possible via flange facings on both ends of the quartz tube. Depending on the gas or gas mixture which is applied these extended light sources [3] are used for the generation of incoherent almost monochromatic radiation of high intensity in the vacuum-UV, UV-C, UV-B and in the UV-A region of the electromagnetic spectrum. Strategic important excimers and their narrow band emissions include the Xe_2^* ($\lambda_{\text{max}}=172 \text{ nm}$), the KrCl^* ($\lambda_{\text{max}}=222 \text{ nm}$), the Cl_2^* ($\lambda_{\text{max}}=259 \text{ nm}$), the XeCl^* ($\lambda_{\text{max}}=308 \text{ nm}$) and the I_2^* ($\lambda_{\text{max}}=342 \text{ nm}$) lamps. The enormous advantage of the innovative excimer technology in photochemical engineering is related to the reactor geometry which can be adapted to the desired photoprocess generating optimal reaction conditions. This opens up outstanding potentialities for water purification technologies and for the realization of preparative and wavelengths selective photochemical transformations.

Our strategy concerning the development of advanced oxidation processes (AOPs [4]) for the treatment of waste waters utilizes the double irradiation in a VUV/UV-excimer flow through photoreactor. The contaminated water is injected into a module which combines the emissions of the KrCl^* and the Xe_2^* -excimer units. Hereby, the VUV-radiation is consumed mainly for water cleavage with efficient formation of hydroxyl radicals and the UV-C output is used for the direct photocleavage of organic pollutants. Most interestingly, the intrinsic formation of hydrogen peroxide *and* of ozone by the VUV-

photolysis of air-saturated water and the wavelengths dependent changes of their concentrations could be detected. Therefore, the novel VUV/UV-oxidation process combines the advantages of the industrial photooxidation technologies (H_2O_2 -UV, O_3 -UV, H_2O_2 - O_3 -UV) in an efficient photoreactor *without* addition of external oxidation agents. The principles, the unprecedented potentials and the economical superiority of the VUV/UV-oxidation technique are demonstrated by the purification of contaminated industrial waters. Examples are waters which contain Rhodamine B, saturated and unsaturated chloro-hydrocarbons, chloro-phenols, Naphtole AS dyes (cotton dyeing), high concentrations of organic carbon (water leakage from a chemical deposit site) or organometallic Ni-complexes (galvanic waste waters). Additionally, the disinfection of greywater and the complete photomineralization of dissolved organic carbon could be manifested. The substrate consumption, the formation of products, the TOC-elimination and the dye-bleaching were monitored by standard analytical methods including GC, HPLC, GC-MS, ion-chromatography, TOC-measurements and UV-spectroscopy, respectively [5].

The most valuable wavelengths dependent industrial process is the photosynthesis of previtamin D (P) by irradiation of 7-dehydrocholesterol (7-DHC). P is the precursor of vitamin D which plays a key role in the regulation of calcium homeostasis. Consequently, we developed an UV-excimer flow through photoreactor which consists of three different excimer lamps with emission maxima at 259 nm, 308 nm and 342 nm [2]. The substrate solution is continuously circulated through quartz tubes which are placed concentrically within the water cooling flow of the UV-excimer sources. With this arrangement the wavelengths selective single or double irradiation of 7-DHC was monitored by HPLC and the production of vitamin D_3 was optimized.

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IN-SITU INFRARED STUDY OF THE INTERFACIAL LAYER DURING THE ANODIC DISSOLUTION OF A SILICON ELECTRODE IN A FLUORIDE ELECTROLYTE

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The anodic corrosion of silicon in aqueous electrolytes is a well-known problem which hinders the use of silicon as a useful material for photoelectrochemistry. As part of a detailed investigation on the anodic dissolution of silicon in fluoride electrolytes, we have studied the infrared (IR) absorption of the p-Si/electrolyte interface in a wide potential range, for fluoride electrolytes of various compositions and pH. This study has been performed using Fourier-Transform IR spectroscopy in the subtractive mode and the potential-modulation mode.

Subtractively-normalized FTIR spectroscopy allows one to follow the interface composition as a function of potential, in parallel with recording of the interface current. Upon increasing the potential, the current first exhibits a steep rise near 0 V_{SCE} and a first maximum, beyond which the interface appears essentially hydroxylated (hydroxide or "wet" oxide). A second current maximum occurs beyond this first current plateau, at potentials around 1.5-2.5 V_{SCE}. A true "dry" oxide layer, characterized by νSiO absorption bands in the 1050-1250 cm⁻¹ region, appears to develop essentially in the region of the second plateau following the second current maximum. It is inferred that the dry oxide is located just against the silicon substrate, and the wet oxide is in contact with the electrolyte. The thickness of the dry oxide is of the order of 50-100 Å and increases with increasing potential. For a given potential, it appears larger for the smaller fluoride concentrations in the electrolyte.

Potential-modulated IR spectroscopy provides improved sensitivity and shows that the initial rising part of the voltammogram takes place at a fully hydrogenated silicon surface (νSiH mode at ~2100 cm⁻¹). It also allows to determine the amount of holes accumulated near the interface. It appears that free-hole accumulation remains weak in the potential region associated to the first current plateau, but becomes very large beyond the second current maximum. This suggests that the limiting step for electron transfer is availability of holes at the surface for the first-plateau region, and availability of trapping sites in the oxide, for the second-plateau region.

For potentials in the second-plateau region, the current tends to exhibit low-frequency damped oscillations, which can be made sustained using a small periodic potential excitation at the resonant frequency. Recording of the IR spectra during the oscillations allows one to obtain, quantitatively, the variation of thickness of the different layers through an oscillation period. Especially, it is found that the thickness of the dry oxide may vary by as much as 30 Å. This suggests that the mechanism responsible for this oscillating behaviour may be connected with the formation/dissolution mechanism of this dry-oxide layer.

PHOTOLYSIS OF HETEROCYCLIC PESTICIDES

CYRIL PARKANYI and DONG CHEN

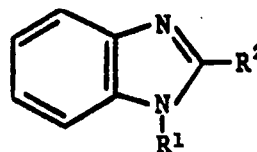
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The various factors determining the fate of pesticides in soil and water systems include, but are not limited to, chemical, microbial, and photochemical decomposition, adsorption, volatilization, movement, and organism uptake. Among these factors, photodegradation of pesticides plays an important role in regions with high insolation. Our previous work in this area includes a study of the bactericides and fungicides 2-mercaptobenzothiazole and 2-mercaptobenzimidazole, and the photolysis of the uracil-based herbicides represented by bromacil and terbacil (two additional herbicides in this series are isocil and lenacil).

As a continuation of our systematic studies of the photodecomposition of pesticides, we have investigated three benzimidazole-based fungicides: benomyl, **1** (Benlate^R, DuPont), thiabendazole, **2** (TBZ, Mertect^R, Merck Sharp & Dohme), and fuberidazole, **3** (Voronit^R, Bayer). Thiabendazole is also a widely used anthelmintic. Cambendazole is an additional closely related fungicide; it is a thiabendazole with an NH.COO *i*-Pr substituent in the benzene ring. Uv irradiation of **1-3** in various solvents (e.g., chloroform, methanol) leads to a number of photodecomposition products. Some of them have been isolated and identified and will be discussed.



1, R¹ = CONH-*n*-Bu, R² = NHCOOMe

2, R¹ = H, R² = 4-thiazolyl

3, R¹ = H, R² = 2-furyl

NONRESONANT TRANSFER EXCITATION COLLISION OF Ca^{17+} WITH He

BY
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ABSTRACT

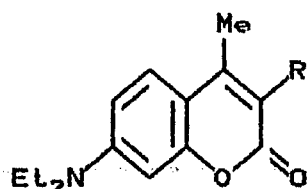
Ion-atom collision processes in which transfer of a target electron to the projectile ion, and at the same time excitation of the projectile (TE) take place, have been the subject of much experimental and theoretical studies in the last decade. The nonresonant transfer excitation (NTEX) cross sections for the collision of the Ca^{17+} with He are calculated. In NTEX, it is assumed that the core of He target causes the excitation of Ca^{17+} projectile with a simultaneous transfer of an electron from He to Ca^{17+} . The resultant excited Ca^{16+} is then relaxed by the emission of X-rays. It is found that, NTEX process for the collisional system takes place in the energy range $E_L = 10\text{-}160$ MeV while its complementary process, RTEX, starts at higher energy $E_L > 140$ MeV. In contrary to the RTEX trends, the NTEX cross section is found to decrease with increasing the atomic number of Li-like ions. A general formula for the radial part of the excitation probability from 1s to np states is successfully developed.

EXCITED STATE DEACTIVATION OF CROWNED 7-AMINOCOUMARINS

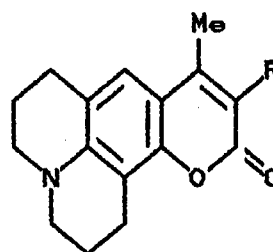
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Photophysics of 3-substituted coumarin 1 (Ia-Im) and 10-substituted coumarin 102 (IIa, IIb) in MeOH has been studied. These compounds have an iso- π -electronic structure and the substituents are nonconjugated with π -system.



I



II

At the protonation of Ib, Id, If, Ih, Ij, Il and IIa the red shift of absorption (ν_a , 600-1000 cm^{-1}) and fluorescence (ν_f , 300-600 cm^{-1}) spectra is observed (Table; see Ic, Ie, Ig, Ii, Ik, Im and IIb). Fluorescence quantum yield (ϕ) of protonated derivatives of coumarin 1 is less than that of neutral forms (except Ih), and ϕ of IIb is greater than ϕ of IIa. In series of neutral crowned derivatives of coumarin 1 (Il, Ij, Ih) value ϕ decreases as the size of crown-cycle diminishes, but in similar series of protonated ones (Im, Ik, Ii) ϕ is not changed practically. The influence of structure and electric field of nonconjugated substituent on the energy level position and deactivation efficiency of excited state of 7-aminocoumarins is discussed.

Table

N	R	ν_a, cm^{-1}	ν_r, cm^{-1}	φ
Ia	H	26640	21850	0.38
Ib	$\text{CH}_2\text{NHCH}_2\text{CH}=\text{CH}_2$	26180	21520	0.74
Io	$\text{CH}_2\text{NH}_2^+\text{CH}_2\text{CH}=\text{CH}_2$	25440	21260	0.21
Id	$\text{CH}_2\text{NHCH}_2\text{Ph}$	26140	21510	0.70
Ie	$\text{CH}_2\text{NH}_2^+\text{CH}_2\text{Ph}$	25420	21180	0.21
If	$\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$	26120	21660	0.45
Ig	$\text{CH}_2\text{NH}^+\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$	25230	21230	0.16
Ih	$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2$	26050	21690	0.070
Ii	$\text{CH}_2\text{NH}^+(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2$	25490	21320	0.22
Ij	$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2$	26100	21530	0.25
Ik	$\text{CH}_2\text{NH}^+(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2$	25180	21170	0.20
Il	$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2$	26160	21600	0.55
Im	$\text{CH}_2\text{NH}^+(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2$	25230	21120	0.23
IIa	$\text{CH}_2\text{N}(\text{CH}_2)_{17}\text{Me}$ Me	25260	20820	0.33
IIb	$\text{CH}_2\text{NH}^+(\text{CH}_2)_{17}\text{Me}$ Me	24280	20540	0.64

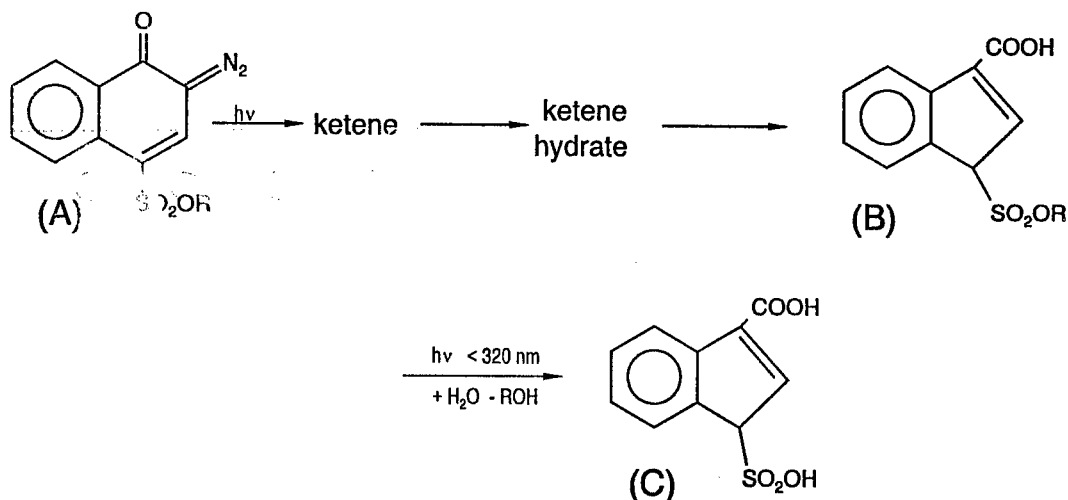
NON-RECIPROCITY PHOTOCHEMICAL BEHAVIOUR OF NEW 1,2-NAPHTHOQUINONE-(2)-DIAZO-SULFONIC ACID ESTERS

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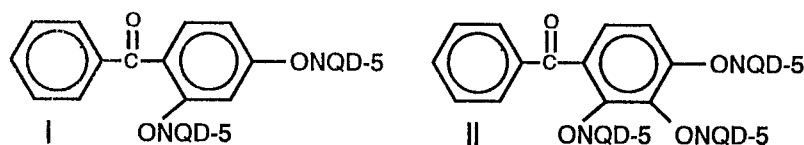
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The 1,2-naphthoquinone-(2)-diazo-derivatives show photolytically induced extrusion of nitrogen and yield indene carboxylic acid via Wolff rearrangement by the addition of water. During photolysis 1,2-naphthoquinone-(2)-diazo-4- and -5-sulfonic phenyl esters show different behaviour. In contrast to the NQD-5-sulfonic isomers, photolysis of the NQD-4-acid esters (B) is accompanied by a photochemically induced ester cleavage. For the reaction the formation of a sulfene intermediate is proposed.



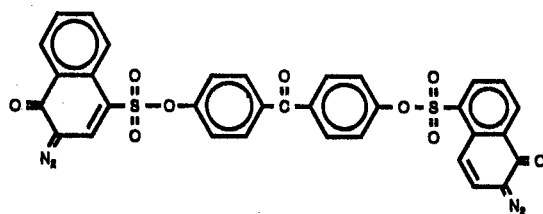
The UV spectra of NQD-4 and NQD-5 chromophors differ. Bi- and trichromophoric NQD systems (I, II) are characterized by a non-reciprocity behaviour.



In this case the photokinetic behaviour is determined by different photolysis rates of the NQD chromophors caused by decreasing reactivity within



Different photochemistry and excitation can be demonstrated by the model compound III. Excitation of III at 405 nm causes a sequential photolysis of both diazo groups, as a result of an energy transfer from NQD-5 chromophore to the NQD-4 chromophore.



III

Tabl. 1 summarises the investigated model compounds. Interactions via sulfonic groups can be excluded by determination of the quantum yields for series I. The dimension of the reaction quantum yield (ser. II, III) indicates an energy transfer between the NQD - chromophors.

	table 1	
<p>ser. I</p> <p>R = NQD-5</p> <p>R' = H, OCH₃, CHO</p> <p>R' = pyridyl, CN</p> <p>R' = m-NO₂, CH(CH₃)₂</p> <hr/> <p>R = NQD-4</p> <p>R' = H, OCH₃, CHO, CH(CH₃)₂</p> <p>R' = CN, O-C₆H₅</p>	<p>ser. II</p> <p>R = R' = NQD-4</p> <p>R = R' = NQD-5</p> <p>R = NQD-4 R' = NQD-5</p>	<p>ser. III</p> <p>R = NQD-4; NQD-5</p>

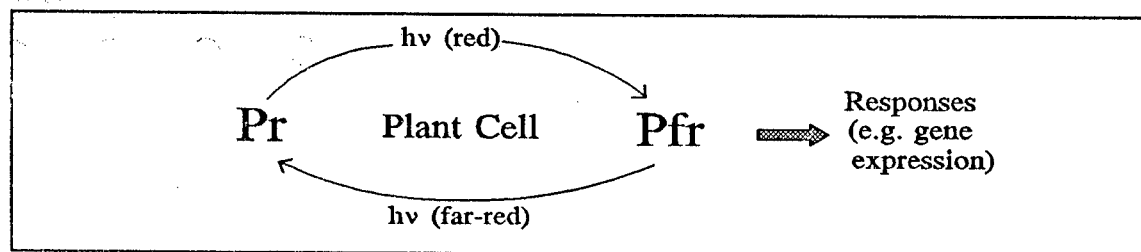
PHYTOCHROME AS LIGHT SENSOR FOR PHOTOSYNTHETIC GENE ACTIVATION

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Using examples from my laboratory, I will discuss how living organisms utilize and interact with visible light as an environmental signal for their growth and development. The lecture will be based on the study of the structure-function relationship of the photo-signal switch phytochrome in higher plants. The specific emphasis of the paper will be to elucidate the structures of the photosensor pigment protein, phytochrome, in photosynthetically active plants. Various biophysical and molecular biological tools have been used to elucidate the structure-function relationship of phytochrome. These are summarized below.

Phytochrome as a Light Switch. Phytochromes mediate light signal transduction processes, such as expression of light-responsive genes (particularly photosynthetically important genes such as *Cab* and *Rubisco*), seed germination, stem growth, and many other developmental and morphogenic photoresponses in plants. Phytochrome functions as red- and far red-light sensors according to the photoreversible scheme shown in the box below.



Light Activation of Phytochrome. Spectroscopic studies of phytochrome are consistent with the Pr → Pfr phototransformation as isomerization. This photoisomerization takes place within a few picoseconds. In many respects, phytochrome can be described as plant's eye pigment.

Pigment-Apoprotein Interactions. Since 1987 we have been studying the structure/conformation of phytochrome in our laboratory. By using the molecular genetic engineering techniques, we are investigating the structural and photobiological aspects of the pigment-protein interactions in the phytochrome molecule. In a recently completed study, we investigated the effects of single amino acid replacements of conserved residues in the vicinity of Cys₃₂₃. We expressed ten site specific mutants of pea phytochrome in Baker's yeast and analyzed them for characteristic phytochrome red/far-red photoreversibility. We found that all ten mutants specifically assembled the chromophore with varying efficiencies. In particular, the His₃₂₄ mutant phytochromes were severely affected, both in their chromophore binding efficiency and the photoreversibility of the reconstituted proteins. Since this residue is located immediately adjacent to the chromophore attachment site, this His-mutagenesis effect can be compared with the neighboring group effect in physical organic chemistry.

Light-Induced Conformational Changes. Several structural domains of phytochrome can be considered as the possible location of "active site(s)". However, the only change in secondary structure detectable by CD seems to occur in the 6-kDa amino terminal segment of the phytochrome molecule, forming amphiphilic α -helix upon Pr \rightarrow Pfr phototransformation. Substitution of the serine residues in the 6-kDa amino terminal segment with alanine forms a more helix favoring sequence, which produced a physiologically hyperactive phytochrome. The amino terminus-truncated phytochrome does not exhibit full biological activity *in vivo*. These results suggest that the amino terminal segment, with its amphiphilic helix-forming sequences, are potential active site(s) for phytochrome function. We are currently investigating the functional implications of the light-induced conformational change in the light-signal transduction cascade in higher plants.

Signal Cascade via G-Proteins? In triggering the transcriptional activation of photosynthetic gene expression in plants, G-proteins likely play a functional role as the molecular transducer of the light signal cascade initiated by phytochrome and red light. We proposed this hypothesis in 1987, and subsequently preliminary evidence was published in 1991. There is growing evidence to support this hypothesis. There is, however, no evidence that phytochrome forms the transmembrane α -helical folds characteristic of most membrane-bound and heterotrimeric G-protein-coupled receptors. But, it is possible that small molecular weight G-proteins transduce at least some of the phytochrome-mediated signal transduction processes. In this vein, we have isolated and purified a 24-kDa small molecular weight G-protein with its properties similar to animal *ras* oncogene products (small molecular weight G-proteins). Initial characterization of the G-protein from oat seedlings has been reported. Characterization of this protein has now been completed and its functional linkage to the phytochrome-mediated signal transduction cascade is being investigated.

Sol-Gel Synthesis and Spectroscopic Properties of Nanoscaled Hybrid Materials

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Sol-gel chemistry and properties of nanoscaled semiconductors are presented. The focus is put on two routes resulting in composite structures of optical quality. The first route, applied to ZnO based materials, yields optically transparent films with controlled morphology and electronic conductivity. Starting precursors of such coatings are particulate sols containing ZnO particles with sizes down to 3 nm. Both the nature of appropriate dopand present in the coating sol and the final sintering conditions employed can strongly affect the nanocrystallite orientation with respect to the substrate. As seen in XRD measurements, the degree of c-axis orientation increases with increasing temperature and the foreign ion size. The specific resistivity of the best ZnO film samples so far, as tested in the microwave absorption studies, has been determined to 0.05 ohm cm.

The second route represents synthesis of hybrid inorganic-organic composites (monolithic bodies or films) with embedded optically active components such as II-VI-quantum dots (f.a. ZnO, CdSe) and/or lanthanide ions. The key component of these glassy polymers are organically modified silanes of the general formula $P-(CH_2)_3-Si(OR)_3$. They contain organic polymerizable functions - P as for example double bonds and inorganic Si-alkoxide ligands. Hydrolysis and condensation of Si-alkoxide groups generates the inorganic silicate network whereas organic polymerisation of double bonds yields the organic polymer part in resulting hybrid matrix. The quantum dot nucleation/growth processes and the ligand environment of lanthanide ions can be controlled by bifunctional molecules of the formula $L-(CH_2)_n-M$, too. L represents a metal complexing function preventing the quantum dots or lanthanide ions to aggregate. The M - group of this spacer carrying either silane or double bond connects these optically active components to the hybrid glass polymer matrix.

The potential of this molecular material processing control is reflected in optical absorption and fluorescence changes accompanying the initial metal complexation steps, the subsequent transition into the wet gel state and their final conversion into a cured (also micro patterned if needed) composite material.

USE OF SOME INDUSTRIAL BY-PRODUCTS
AS ENERGY STORAGE MEDIA

By

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Abstract:

Solar energy is stored using different solid storage materials, both chemical and metallic by-products. The materials tested in the present study are paraffin wax, copper slag, aluminium slag, iron slag, cast iron slag, and copper chips. Solar energy is stored in these materials and the stored energy is next recovered with a water streams at different flow rates and the storage capacity and period for different materials were compared. The same set of experiments is run on solid metallic materials mixed with wax. The results indicated that iron slag has the highest storage capacity followed by cast iron slag then aluminium slag and copper chips and copper slag. It is also noted that addition of paraffin wax to the solid metallic materials improves its storage capacity and duration greatly. The storage efficiency of different units is calculated and compared. It is found that addition of paraffin wax to cast iron slag and to copper chips increases the amount of stored energy by 161.8% and 108.4%, respectively. Moreover, increasing heat transfer fluid flow rate increases the amount of energy that can be extracted in a specified period of time, but it decreases the time of energy extraction (half a cycle).

AN *IN VITRO* MODEL OF PREVITAMIN D PHOTOSYNTHESIS
AS POSSIBLE MONITOR OF SOLAR UVB RADIATION:
KINETIC STUDIES USING TUNABLE LASER

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Biological activity of UVB solar radiation (280-315nm) causes the need of permanent control. This problem is dramatized by ozone depletion effect increasing the amount of UVB radiation reaching the earth surface. Because UVB radiation is only a small fraction of the total solar radiation, an accurate measurement of spectral distribution of UVB radiation at the short wavelength edge of solar spectrum presents a real challenge.

The correlation of the method of UVB dosimetry to the action spectrum of some natural biological process is very desirable in view of a central role which action spectra play in the initial characterization of bioresponses.

Vitamin D synthesis in human skin is considered one of the beneficial effects of solar UVB. In response to the absorption spectrum of initial provitamin D the action spectrum peaks at 280nm dropping to zero at 315nm.

The remarkable feature of the photoreaction *in vitro* is significant dependence of the photoproducts formation on the irradiation wavelength. This fact, along with our close examination of the wavelength effect on the photoreaction kinetics using tunable dye-laser [1,2], allowed us to suggest that the *in vitro* model of previtamin D photosynthesis is just the process which is best suited to the sensitive, accurate and spectrally selective monitoring of solar UVB and ozone depletion effect [3].

To *in situ* follow the photoreaction course we have developed the original express method of spectral analysis of the photoisomer mixture which is strongly promotes realization of the proposal.

Computer simulations of the reaction kinetics for different spectral position of the shortwave edge of solar spectrum simulating both its seasonal changes and ozone depletion effect, confirmed the potential of the photoreaction as spectrally selective monitor of solar UVB, and convincingly showed that, in contrast to a majority of known UVB meters, it was capable of measuring not only integral solar UVB radiation but also its spectral distribution at the shortwave edge. This ability offers a substantial advantage of the method proposed.

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3. I.P.Terenetskaya, SPIE Proceedings, 1994, v.2134.

THE PROBLEM OF LIGHT SOURCE IN VITAMIN D INDUSTRIAL SYNTHESIS: LAMP, LASER OR SUN?

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It is well known that vitamin D is of vital importance for human health being essential for a wide variety of biological responses. Sunlight has long been recognized as a major provider of vitamin D for humans. The UV portion of sunlight converts provitamin D in skin to previtamin D which is thermally converted into vitamin D.

As well vitamins D₃ and D₂ are manufactured by UV irradiation of starting provitamins (7-DHC or ergosterol). Unfortunately, previtamin D photosynthesis *in vitro* is much complicated by the side photoconversions of previtamin. Since the photoisomer mixture composition is dependent on the irradiation wavelength, the maximization of the yield is usually achieved by the proper choice of the excitation source and the irradiation regime.

Our study of the photoreaction kinetics using tunable laser has revealed the unknown earlier effects which strongly restrict traditional methods of the photoreaction optimization [1-3].

Careful examination of the wavelength, laser intensity and pulse duration effects together with computer simulations of the reaction kinetics gave a good indication of the excitation light characteristics on previtamin D photobehaviour [4,5]. On the other hand, the elucidation of a reaction medium effect on conformational state and photoconversion channels of previtamin D molecule gained more understanding of the difference between the *in vivo* and *in vitro* photoprocesses [6-9].

This paper estimates advantages and disadvantages of lamp and laser sources of initiation of the *in vitro* previtamin D photosynthesis. The problem of the natural sun light utilization in vitamin D manufacturing is also discussed.

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PHOTOINDUCED PROTON TRANSFER IN SUBSTITUTED PYRIDINES

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Our laboratory has maintained an interest in the luminescence and excited state behavior of aromatic nitrogen heterocyclics. In particular the ordering of n,π and π,π electronic states determine the excited state properties of these molecules. Our investigations with substituted pyridines have focused on i) aminopyridines, ii) hydroxypyridines and iii) phenylpyridines, all of which undergo an excited state protonation. In the case of the 2-, 3- and 4-phenylpyridine we have shown that it is a necessary condition for fluorescence emission, and increased planarity accompanies the conversion to the triplet state. Phenylpyridines appear to behave as substituted pyridines in the singlet state and as substituted phenyl derivatives in the triplet state. The behavior of 2,6-diphenylpyridine will also be discussed. Results obtained for the absorption and emission of the hydroxypyridines indicate that in 2-pyridone there is a relaxation route involving formation of a C_{2h} dimer. Aminopyridines also undergo an excited state protonation; however, in these molecules the amine hydrogen is involved in rapid quenching of the singlet state. In all cases the experimental results are supplemented by CNDO/S calculations, which indicate that an inversion of the singlet states in acidic media is accompanied by an increasing oscillator strength for the lowest singlet. The molecules investigated show a satisfactory correlation between theory and experiment, and our interpretation is supported by fluorescence quantum yield and lifetime measurements, as well as phosphorescence quantum yield, lifetime and polarization data. Luminescence data measured in different solvents will be presented together with the electronic state diagrams obtained from the CNDO/S calculations of these molecules.

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Excited-state Proton Transfer in Constrained Environments

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Hydroxyarenes undergo a remarkable shift in acidity (Förster shift) upon photoexcitation. For simple hydroxyarenes such as 2-naphthol, this shift is in the range of 7 pK_a units, i. e., from 9 to 2, and allows the study of proton-transfer dynamics by time-resolved spectroscopy. Most studies have concentrated on the structure of water as the key variable in controlling the rate of proton transfer. We have constructed a number of naphthols in which functional groups of varying proton affinity are attached through an alkyl chain. This allows us to investigate the dynamics of intramolecular proton transfer in which the structure of the solvent still plays a key role. By reducing the entropic requirements for solvent reorganization during the proton transfer step, intramolecular proton transfer is accelerated relative to the intermolecular case. In contrast, the photoinduced cyclization of 1-allyl-2-naphthol is shown to occur by free-radical mechanism.

EXCITED STATE PROTON TRANSFER LASERS

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The review of lasers using inter- and intramolecular excited state proton transfer reactions (ESPT) is given. The general principles of ESPT lasers are considered. The criteria for acid-base system selection of active media ESPT lasers are stated. They can be used for purposeful synthesis of organic compounds for active media of ESPT lasers.

The regularities of intramolecular ESPT lasers and intermolecular ESPT lasers based on oxy-, amino-, oxo-, and azaaromatic compounds are analyzed. The possibility of simultaneous lasing of both acid-base components and wide tuning lasing range of acid-base systems including these compounds are considered. The mechanism of mutual negative influence of conjugated acid-base components on their lasing effect is discussed. This influence results in the impossibility of simultaneous lasing of both forms of azaaromatic compounds.

The short-lived intermediates formed in photochemical electron transfer reactions in laser active media play an important role in lasing efficiency. The active media photostability of ESPT lasers and the effect of medium acidity and basicity on the lasing solution degradation are considered. The photostability and efficiency of active media can be improved by some additives to lasing solutions.

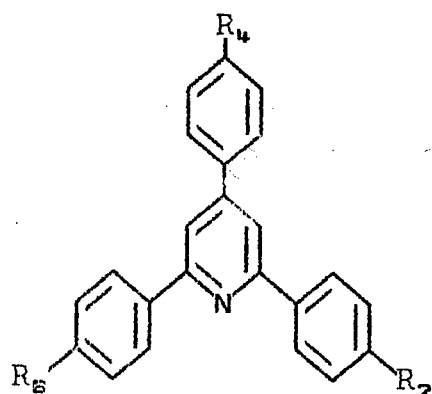
The acid-base systems provided the wide tuning lasing range are analyzed. Using of binary dyes solutions to get a wide tuning range as a useful approach for inter- and intramolecular ESPT lasers is discussed.

RADIATIONLESS DEACTIVATION AT INTERMOLECULAR EXCITED STATE PROTON TRANSFER OF 2,4,6-TRIARYLPYRIDINES

Uzhinov B.M., Dmitrouk S.L. and Druzhinin S.I.

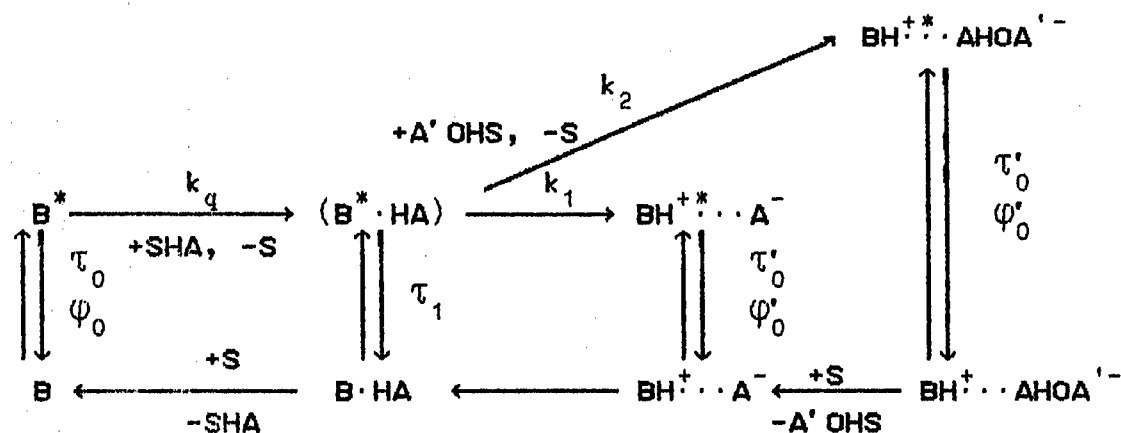
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The intermolecular excited state proton transfer (ESPT) of 2,4,6-triarylpyridines (TAPs) with carboxylic acids in solvents of different polarity and basicity has been studied by absorption and fluorescence spectroscopy and kinetic fluorometry.



TAP	R ₂	R ₄	R ₆
246PhPy	H	H	H
26Ph4AnPy	H	OCH ₃	H
24An6PhPy	OCH ₃	OCH ₃	H
26An4PhPy	OCH ₃	H	OCH ₃
246AnPy	OCH ₃	OCH ₃	OCH ₃

The ESPT of TAP proceeds via dynamic mechanism and results in the formation of TAP cation protonated at pyridinium nitrogen atom. The ESPT reaction induces the radiationless deactivation of excited molecules. The quantum yield of excited product in the ESPT reaction (ϕ_r) is less than unity. The ϕ_r value increases as TAP basicity and medium acidity (carboxylic acid concentration) increase. Two-step reaction scheme is proposed for explanation of ϕ_r behaviour. At first step the intermediate nonfluorescent complex is formed by interaction of one solvated acid molecule (SHA) with molecule of TAP (B). The excited TAP monocation is formed by monomolecular proton transfer in this complex (k_1) and by addition of second molecule of proton donor to this complex (k_2).



According to this scheme ϕ_r value is determined by specific solvation of excited state reaction products. The rising of ϕ_r value at increasing of TAP basicity and medium acidity is caused by increasing of proton transfer rate in intermediate complex as a result of decreasing of product formation free energy. The concentration dependence of ϕ_r in various solvents is described quantitatively by this scheme. The fluorescence data of triarylpiperidines and kinetic characteristics of their interaction with CH_3COOH in dioxane are given in Table.

Table

TAP	λ_r	λ'_r	ϕ_0	ϕ'_0	ϕ_r^a	$k_q\tau_0$	$k_2\tau_1$	$k_1\tau_1$	$K,^b$	lgK^*
	nm		%			M^{-1}			M^{-1}	
246PhPy	363	405	45	24	<1	0.17	0.004	<0.001	0.78	4.7
26Ph4AnPy	360	456	39	33	9	0.22	0.033	<0.001	4.45	7.7
24An6PhPy	373	481	41	54	26	0.42	0.139	<0.001	6.10	10.2
26An4PhPy	374	466	33	88	38	0.31	0.104	0.015	19.7	10.3
246AnPy	368	462	49	65	62	0.69	0.314	0.641	117.4	10.5

^a $[CH_3COOH] = 3 M$,

^b K - equilibrium constant of TAP protonation by CF_3COOH

Triplet State Radical Cleavage of Ring Halogens from Phenyl Ketones: Different Modes for Different Electronic States

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UV irradiation of several iodo- and bromophenyl ketones in solvents containing reactive C-H bonds or added thiol results in the dehalogenation of the halophenyl ketones. Quantum yields range from 5-50%; their dependence on solvent viscosity reveals significant amounts of cage recombination. Rate constants for radical cleavage of the ketone triplet states were measured by steady state techniques and by direct laser flash kinetics for the ortho, meta and para isomers of three sets of halophenyl ketones. For bromo ketones, rate constants are comparable for the meta and para isomers ($\sim 10^8 \text{ s}^{-1}$ for the acetophenones and $\sim 10^5 \text{ s}^{-1}$ for the benzophenones) but larger for the ortho isomers (5×10^8 and 10^7 s^{-1}); for the iodobenzophenones, rate constants are $>10^{10}$, 3×10^9 , and $3 \times 10^7 \text{ s}^{-1}$ for the ortho, para, and meta isomers, respectively. Activation parameters for the bromoacetophenones are: $\Delta H^\ddagger = 5.7 \text{ kcal/mole}$, $\log A = 12.0-12.4$. For the iodobenzophenones, $\Delta H^\ddagger = 4.0 \text{ kcal/mole}$; $\log A = 10.5$ meta and ~ 12 para.

It is suggested that the triplet iodobenzophenones undergo $\sim 4 \text{ kcal/mole}$ exothermic cleavage by an activated conversion of their n, π^* triplets into dissociative σ, σ^* states. This interconversion seems to be driven by π^* electron density, which is much higher para than meta. The bromoketones undergo 6-10 kcal/mole endothermic cleavage, apparently primarily from π, π^* triplets that have strong bromine-to-carbonyl charge transfer components. This CT character is comparable for both meta and para isomers and fosters conversion into $\pi(\text{Br}), \sigma^*$ states. In this model for cleavage the apparent negative activation entropies in fact represent variable low efficiencies for interconversion between the low energy nondissociative excited states and the higher energy dissociative ones. It is suggested that direct charge transfer from halogen to carbonyl may be involved with the ortho-halo ketones.

**INJECTION AND DISCHARGE OF PHOTO-GENERATED CHARGE
CARRIERS AT THE SEMICONDUCTOR/ELECTROLYTE
INTERFACE**

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Catastrophic Polarization of Twisted Excited States

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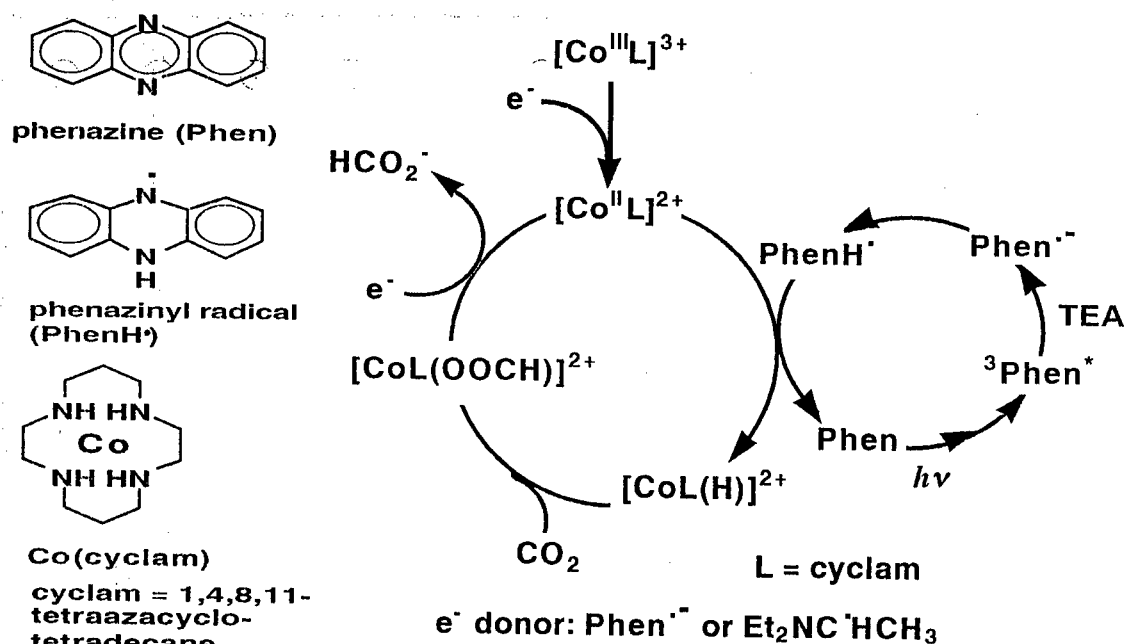
In 1971 it was proposed that when a pi-electron absorbs a photon and begins a cis-trans conversion it passes through a twisted state that is extremely polarizable. The current state of knowledge of such twisted states will be set forth and several conjectures will be discussed.

PHENAZINE-PHOTOSENSITIZED REDUCTION OF CO₂ MEDIATED BY COBALT-CYCLAM COMPLEX

Shozo Yanagida, Tomoyuki Ogata, Yoshie Yamamoto, Yuji Wada, Kei Murakoshi, Mitsuhiro Kusaba, Nobuaki Nakashima, Akito Ishida, and Setsuo Takamuku

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Photoreduction of carbon dioxide (CO₂) to formate (HCO₂⁻) can be achieved by UV-irradiation of the system involving phenazine (Phen) as a photosensitizer, triethylamine (TEA) as an electron donor, and cobalt-cyclam complex (Co^{III}L, L = cyclam = 1,4,8,11-tetraazacyclotetradecane) as an electron mediator. Reduction products from the system are HCO₂⁻, and a small quantity of CO and H₂.



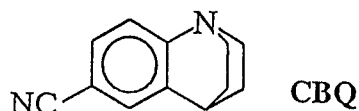
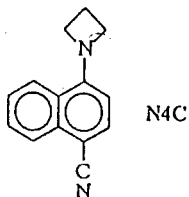
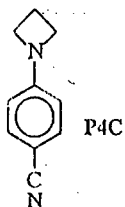
Preferential electron transfer from the photoformed radical anion of phenazine (Phen^{•-}) to Co^{III}L is confirmed by ESR analysis and pulse radiolysis. The resulting Co^{II}L undergoes hydrogen transfer from phenazinyl radical with a second order rate constant $k \approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$, giving [CoL(H)]²⁺. The effective insertion of CO₂ molecule into [CoL(H)]²⁺ yields HCO₂⁻ selectively. This shows a good example for the utilization of profitable capability of nitrogen-containing aromatics, which have a function not only of electron transfer but also hydrogen transfer through a semiquinone radical.

INFLUENCE OF ENERGY GAP $\Delta E(S_1, S_2)$ and AMINO N-INVERSION IN INTRAMOLECULAR CHARGE TRANSFER. DUAL FLUORESCENCE AND SINGLE CT-EMISSION.

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The phenomenon of dual fluorescence in a series of four 4-aminobenzonitriles in which the amino nitrogen atom is part of a four- to seven-membered heterocyclic ring, P4C to P7C, is investigated by using time-resolved measurements. The rate constant k_a of excited state intramolecular charge transfer (ICT) in e.g. diethyl ether strongly decreases with decreasing ring size. With P4C in diethyl ether ICT does not occur. This is attributed to the corresponding increase in the amino nitrogen inversion barrier, which is considered to be an important reaction coordinate in the ICT process. Similarly, dual fluorescence and ICT is absent with N4C, an 1-amino-4-cyano-naphthalene with a 4-membered heterocyclic ring. This is the case irrespective of solvent polarity.



On the basis of these results and other experiments treated elsewhere [1,2], it is suggested that for the occurrence of ICT and dual fluorescence in aminobenzonitriles two requirements have to be fulfilled: (1) a sufficiently small energy gap $\Delta E(S_1, S_2)$ between two interacting excited states ($S_1(^1L_b)$ and $S_2(CT)$), and (2) the presence of a promoting mode such as nitrogen inversion. When the order of the 1L_b - and CT -states is reversed and $\Delta E(S_1, S_2)$ increases in magnitude, such as with 6-cyanobenzoquinuclidine (CBQ), dual fluorescence no longer occurs. Instead, a single fluorescence is observed, emitted by the now lowest $S_1(CT)$ -state.

It is further argued that the solvent-induced pseudo-Jahn-Teller mechanism causing the ICT and dual fluorescence in 4-(dimethylamino)benzonitrile (DMABN) and related molecules does not operate in biaryls such as 9,9'-bianthryl, where the thermodynamic reaction requirements are similar to those holding for exciplexes.

[1] W. Schuddeboom, S. A. Jonker, J. M. Warman, U. Leinhos, W. Kühnle, and K. A. Zachariasse, *J. Phys. Chem.* **96** (1992) 10809.

[2] K. A. Zachariasse, Th. von der Haar, A. Hebecker, U. Leinhos, and W. Kühnle, *Pure & Appl. Chem.* **65** (1993) 1745.

DIPOLE-DIPOLE AND EXCHANGE ENERGY TRANSFER IN DIFFERENT TYPES OF PORPHYRIN CHEMICAL DIMERS

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Well-defined covalently linked molecular assemblies of chlorophylls, porphyrins and other reactants are very suitable objects for modelling and study of primary photoprocesses *in vivo* such as electronic excitation energy transfer and electron transport. In this report we discuss the results of experimental and theoretical investigation of energy transfer processes at 1.8 - 300 K in chemical dimers of porphyrins, chlorins and their Me-complexes (Zn, Cu, Ni) with different spacers between macrocycles (-CH₂-CH₂- bond, methyne bridge, phenyl ring) which have been synthesized in our laboratory. The main conclusions are the following:

1. Dipole-dipole interactions of weak Q-transitions ($V_{12} = 6 + 11 \text{ cm}^{-1}$) in porphyrin dimers lead to intracomplex singlet-singlet energy transfer (ET) with probabilities $F^{SS} = 5 \cdot 10^8 + 4 \cdot 10^{10} \text{ s}^{-1}$ without quantum losses. The effective S-S ET is essentially temperature dependent and its dynamics at 77 - 300 K is fully described by Forster- Galanin theory of inductive resonance. In the case of Zn-chlorin dimers the splitting of B- and Q-bands in absorption spectra is due to excitonic interactions ($V_{12} = 950 - 240 \text{ cm}^{-1}$) between macrocycles at intercenter distances $R = 0.6 - 1.1 \text{ nm}$.

2. For Cu-cyclopentaneporphyrin dimers with $R = 1.23 \text{ nm}$ the exchange triplet-triplet ET is realized with the probability value $F^{TT} = 2 \cdot 10^8 \text{ s}^{-1}$. At the weakening of dipole-dipole interactions (transition to free base cyclopentaneporphyrin dimers) the effective exchange S-S ET takes place ($F^{SS} \approx 10^9 \text{ s}^{-1}$). In hybrid ethane-bisporphyrins with transition metal ion Ni in the center of one half of the dimer conformational dynamics of macrocycles around -CH₂ - CH₂- spacer depending on temperature and solvent nature plays the essential role in exchange ET from porphyrin macrocycles to low lying d-levels of Ni ion ($F \approx 10^{11} \text{ s}^{-1}$). For such type dimers with Cu ion the exchange d- π effects manifest themselves in the increase of the intersystem crossing probability by 1-2 orders in the covalently linked neighbour.

3. On the basis of site-selection and hole burning experiments for symmetrical ethane-bisporphyrins at 1.8-51 K it has been demonstrated that pair interactions between covalently linked chemically identical macrocycles in the conditions of their essential spectral non-homogeneity manifest themselves in specific spectral effects: the narrowing of Q(0,0) fluorescence band in comparison with monomeric one, the splitting of fluorescence excitation Q(0,0) band into to subbands with quasilinear structure and the dependence of the hole half-widths on the excitation wavelength. From spectral hole burning data the experimental probability of S-S ET is estimated by the value $F^{SS} = 10^{11} \text{ s}^{-1}$. It has been shown that in glassy matrixes at low temperatures (<70 K) the usual calculations of spectral overlapping integrals according with inductive resonance theory are not applicable.

Certain experiments described in this report have been partly supported by the Foundation of Fundamental Investigations of Belarus (No Ph5-111) and by Grant No RW 1000 from the International Science Foundation.

ENERGY AND ELECTRON TRANSFER PROCESSES IN SELF-ORGANIZED PORPHYRIN AND CHLORIN TRIADIC AND PENTADIC COMPLEXES

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Inspired by the determination of the three-dimensional architecture of photosynthetic reaction centers many tetrapyrrole-based synthetic models have been prepared to develop an efficient synthetic catalyst for electronic excitation energy transfer and photoinduced charge separation. Here we report the structural and optical properties as well as the regularities of primary photoprocesses in artificial self-organized trimeric and pentameric complexes formed by two-fold coordination of di-pyridyl and tetra-pyridyl substituted porphyrins or related molecules with Zn-porphyrin and Zn-chlorin covalently linked dimers [(ZnTPP)₂, (ZnHTPP)₂, (ZnOEP)₂, (ZnOECh)₂] having various spacers (-CH₂ - CH₂- bond or phenyl ring). The systems under consideration have been studied by use of steady-state fluorescence and absorption spectroscopic methods as well as a fluorescent picosecond laser setup ($\Delta t = 30$ ps) with 2-D (wavelength-lifetime) registration in methylcyclohexane solutions in a temperature range from 140 K to 360 K.

Spectral transformations of Zn-dimers absorption upon the complexation with di- and tetra-pyridyl containing π -conjugated macrocycles (red shift of Q- and B-bands up to $\Delta\nu \approx 550$ cm⁻¹ and changes of the relative intensities of dimeric Q(0,0) and Q(0,1) bands) are due to the extra-ligation effect. The splitting of Zn-dimer Soret bands ($\Delta E \geq 600$ cm⁻¹) and appearance of complicated splitted spectral manifolds with $\Delta\nu \leq 1900$ cm⁻¹ in pentameric complexes are connected with excitonic interactions of strong resonant B-transitions of π -conjugated macrocycles. Observed experimental splittings are compared with theoretical calculations on the base of the point dipole approximation and computer-simulated architecture of the complexes under consideration. On the basis of absorption and fluorescence data at different temperatures and various ratios of interacting components the complexation constants (K_c) have been estimated ($K_c = 2 \cdot 10^6$ to $6 \cdot 10^7$ M⁻¹ for triads and pentads) as well as the activation energies have been evaluated ($E_A \approx 0.6 + 1.0$ eV).

Picosecond time-resolved experiments reveal that fast forward and backward nonradiative S-S energy transfer (with probabilities of $>10^{11}$ s⁻¹ and $\sim 10^{10}$ s⁻¹ correspondingly) is the most essential path of energy deactivation of Zn-porphyrin dimers within triads and pentads. Transitions to low-lying charge-transfer states with probabilities of order $10^8 + 10^9$ s⁻¹ are considered as an origin of ligand emission quenching within complexes in some cases. In the case of [2(ZnHTPP)₂+CuP(m-Pyr)₄] pentameric complex the increasing probability of intersystem crossing ($\tau > 10^{11}$ s⁻¹) in Zn-dimer due to exchange d- π effect of ligand Cu ion and thermally activated ($\Delta E = 460$ cm⁻¹) energy transfer play the essential role in electronic excitation energy deactivation processes. For self-organized porphyrin-quinone tetrads it has been shown that the energy transfer is faster than 10 ps and is thus competitive with electron transfer which occurs on a 500 ps time scale. Both photoinduced processes within the assemblies are strongly dependent on temperature and solvent polarity.

Financial support of this investigation from Volkswagen-Stiftung (No 54753-61) is gratefully acknowledged, certain experiments have been supported by the Foundation of Fundamental Investigations of Belarus (No Ph5-111).

RECENT ADVANCES IN MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY.

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Our recent research has pursued several directions. One is the photochemistry in constrained media, this includes crystal lattices and molecular spiderwebs consisting of polymeric matrices. It has been long known that photochemistry in crystalline media often proceeds differently than in solution. With the exception of the "Cohen Proximity Rule" for bimolecular cycloaddition of two π bonds, theoretical treatments have been lacking. Our efforts have been both experimental and theoretical and have focussed on unimolecular rearrangements. For a variety of reactions the experimental behavior has proven to be understandable on a quantitative basis.

Least motion at the "branch point" of a reaction is controlling in polymeric media while reactant motion in crystal lattices is best understood quantitatively on the basis of possible motions and energy change in the irregular crystal lattice cage. Least motion, overlap measurements, and molecular mechanics on such imbedded molecules -- are described. Not only can one predict the direction of reactivity in a given crystal, but also one can predict when a crystal lattice will inhibit reaction. When a reaction does occur, the reaction course corresponds to (a) minimum overlap of the transition structure with the surrounding lattice, (b) least motion of the reactant molecule in proceeding to the transition structure, and (c) minimum energy of the geometry optimized transition structure in the host crystal lattice.

In other efforts, we have investigated, experimentally and theoretically, the behavior of 1,4- and 1,3-diradical species involved in the Di- π -Methane rearrangement. Independent generation of some of the species along different reaction coordinates establishes these as thermally equilibrated intermediates. Evidence is presented for two triplets (T1 & T2) for naphthobarrelene as well as for the cyclopropyldicarbonyl intermediate.

In connection with our research on diradicals, we have investigated triplet hypersurfaces at an ab initio level. For the rearrangement of barrelenes it turned out that the energy minima corresponding to the two diradicals intrude on the S0 hypersurface equally. Yet the evidence is that only one of the two T1 diradical minima is utilized in intersystem crossing to ground state. Spin-orbit coupling computations, however, account for the differing rates of ISC. Furthermore, a dissection of spin-orbit coupling into local contributions has been developed, thus permitting one to analyze the source of the overall effect.

**Improvement of Hydrogen Generation by surface modification of
semiconductor electrode**

M. Abdel Fattah, . S. Aly

*Higher technological Institute
10th of Ramadan*

Abstract

The improvement of hydrogen evolution from two different types of catalyst p-type photo cathodic surfaces has been examined. p-type Si has been platinized by photo-electrochemically plating on to the Si surface. Such a photo cathode shows significant improvement (compared to naked p-type Si) for photo chemical H₂ evolution with respect to output photo voltage and overall efficiency.

A second kind of H₂ evolution catalyst has been confined to the surface of p-type Si.

Nickel have been confined to the surface.

Such a surface is again significantly improved compared to naked p-type Si with respect to H₂ evolution.

Experiments with different conditions confirm an important difference in the mechanism of H₂ evolution catalysis for the two surface catalyst systems.

A model for the current - voltage curve of photo-excited silicon electrode

M. Abdel Fattah, .: S. Aly

Higher technological Institute

10th of Ramadan

Abstract

A model to describe the behavior of photo-excited electrodes in a photoelectrochemical cell (PEC) is developed. In addition to the bulk semiconductor properties, the important parameters are the charge transfer rate constant at the interface across the interfacial barrier, the surface recombination rate constant and the bulk recombination rate constant. Using experimental curves for hydrogen evolution at p-type Si electrode show that the I-V curve in cathodic bias is controlled by the competition between the above factors.

Formation of 1,1-Dimethy 1- γ -Cyanine Iodide From Quinaldinium Methiodide under Solar and Ultraviolet Illumination

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Quinaldine methiodide has been photolysed in ethanol and in aqueous solution. 1-Methy 1-1,2-dihydro-(1-methy 1-1,2-dihydro-2-quinolinylyden)-2-quinoline iodide has been obtained in low yield upon photolysis using a high pressure mercury vapour lamp, as well as by sunlight irradiation. Steady-state photolysis has been carried out in ethanol, water and EPA at room temperature and 77k. The mechanism and spectral data will be discussed.

FLUORESCENCE PROPERTIES OF EMODINE DERIVATIVES

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Zagazig University, Zagazig - Egypt.

Fluorescence properties of emodine derivatives, such as 3-methyl-1,6,8-trihydroxyanthracene-9,10-dione, 3-bromomethyl-1,6,8-triacetyloxyanthracene-9,10-dione; 1,3,8-trihydroxy-6-octyloxymethyl anthracene-9,10-dione; 3-hexadecyloxymethyl-1,6,8-trihydroxy-anthracene-9,10-dione; 3-(2,3-dihydroxy propoxymethyl)-1,6,8-trihydroxyanthracene-9,10-dione and ω -triethyleneglycolyl-emodine has been discussed.

OPTIMIZATION OF METAL THICKNESS USED IN SCHOTTKY BARRIER SILICON SOLAR CELL

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Physics Department, Faculty of Science, Assiut, University,
Assiut, Egypt.

Abstract

Experimental results are reported concerning the barrier metal thickness effects on the performance of the Schottky barrier solar cells, which were fabricated using a semitransparent Cr-Cu-Cr barrier metal layer on p-type Si single crystal. The ideality factor and the barrier height of the devices doesn't show any change with the Cu layer thickness. The results are in agreement with the Auger Electron Spectroscopy investigations. This work proved that there is no Cu diffusion into the Si substrate in these structures.

OPTICAL STUDIES OF SOME DYES AS LUMINESCENT SOLAR COLLECTORS

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ZAGAZIG, EGYPT**

Spectroscopic characteristics of Rhodamine B (RB) and Rhodamine 6G (R6G) used as luminescent solar concentrators (LSC) have been studied. The high photostability of RB dissolved in Triton X-100 plus 10% ethanol in outdoor tests could serve as suitable liquid solution LSC. RB and R6G doped in polymethylmethacrylate (PMMA) gave good stability in outdoor tests. The results are compared with others set of measurements on some commercially available dyes used as LSC.

Study of the Incoming Infra-Red (IR) Solar Radiation at Cairo, Egypt

by

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University, Egypt.

Physics Department , Faculty of Science Zagazig University, Egypt

Abstract :-

Measurements of incoming monthly Infra-Red (IR) solar radiation were Carried out at Cairo for three years, period from 1990 to 1992. Hourly data for complet one year were also measured, using Epply Pyer-Geometer, by the Egyptian Meteorological Authority. Global and diffuse solar radiation were recorded for the same period using Epply Pyranometer. all the meteorological parameters were also collected for the same period and site. These data were treated using an advanced computer program to obtain the numerical values of the regression and corrlation coefficients relating the incoming IR radiation with the other meteorological weather parameters such as Screen Temperature (T), Water Vapour Pressure (e), and Surface Clouds (SC). A recommended correlation equations were also found. The ratio of the IR to the global solar radiation (IR/G) ranged between 4.4% in winter and 2.7% in summer.

Our recommended correlation equations can be used with confidence to calculate the IR fraction of solar radiation ,from easily measured weather parameters, which is important for many agricultural and Engineering applications.

STUDIES ON ANODIC DISSOLUTION OF SILICON ELECTRODES IN FLUORIDE MEDIA IN DARKNESS AND UNDER ILLUMINATION

Hamdy H. HASSAN¹*, J.-L. SCULFORT¹, B. FOTOUHI¹, M. NEUMANN-SPALLART² and M. ETMAN¹

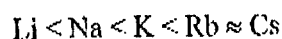
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Preliminary results obtained by Mr HASSAN have been already the subject of a previous communication in the 2nd Meeting of this congress in January 1993. New interesting results will be presented in this Meeting. With the new results, Mr HASSAN has confirmed that the anodic dissolution process of p-Si in fluoride media is a mixed controlled process. Koutecky-Levich analysis allowed the separation of the kinetic and diffusion contribution in the measured current. While for low nominal fluoride concentrations the process was revealed to be mainly kinetically-controlled, for high fluoride concentrations, it is mainly a diffusion controlled one. There is a critical nominal fluoride concentration, C_F^* , for which kinetic and diffusion contributions are of equal importance. This critical concentration depends on pH, rotation rate and electrode potential. Contrary to the kinetic current, the diffusion current seems to be almost constant for polarizations higher than the potential of the generation of porous silicon corresponding to the current J_1 on the typical current-potential characteristics (represented in the lecture) and insensitive to pH in the range of $0 < \text{pH} < 4$.

For low C_F values, while the diffusion current varies proportionally to C_F , the kinetic and measured current change proportionally to C_F^α (with $\alpha \approx 2-2.5$). At limiting C_F values, deviations from these relations towards lower C_F exponents appear. The limiting concentration values are higher for J_3 and J_4 than for J_1 and J_2 .

The effect of alkali-metal and some quaternary ammonium cations on the anodic dissolution of p-Si in fluoride media has been also studied. Dissolution current has been noticed to depend considerably on the nature of the supporting electrolyte and the influence was revealed to be mainly due to cations. The measured current was found to increase in the order:



While the diffusion current seems not to be sensitive to cations, kinetic current appears to change considerably and leads to an important increase of the critical fluoride concentrations, C_F^* , from Cs to Li, for a given pH.

When n-Si electrodes are concerned, holes are the minority carriers and silicon dissolution will be accelerated when the reversely biased interface is illuminated. The rate determining

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step for an electrochemical dissolution process is determined either by charge-transfer process or by mass-transport processes according to the number of holes available at the electrode surface. If only few holes are available at the electrode surface, the trench tips, are more effective in collecting them and the trench growth is favoured, even if initially the electrode was smoothly polished. In this case, the rate determining step is the charge-transfer process.

In the case of high light intensity, the trench will be less effective in collecting holes than the electrode interface does. The etch rate inside a trench is then smaller than the etch rate of the surface ; only in this case, the electrode surface will be flat after some time and favour the rapid passage of holes. This effects is utilized for smoothing out surfaces and contributes to excellent electropolishing. The rate determining step is the mass-transport process.

INTEREST OF IMPEDANCE SPECTROSCOPY TECHNIQUES FOR CORROSION MECHANISM INVESTIGATIONS

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Impedance of a given system corresponds to a relation between the output response and the perturbing input signal. The perturbing signals could be galvanostatic, potentiostatic, hydrodynamic, optic, etc... and can be imposed either as a pulse or as a sinusoidal wave. The response of the perturbed system then appears as transient or stationary signals.

Chemical and/or electrochemical processes are characterized by one or more time constants. The associated responses depend on the frequency of the imposed perturbation sources. The impedance techniques, contrary to the steady-state ones, lead to information on all occurring processes either in the bulk of liquids or solids or at the solid/liquid interface whatever the nature of the studied material is.

The advantages of impedance techniques are numerous. One of the essential advantage concerning pulse impedance technique consists in obtaining in a very short time, the response of the system in a very large domain of frequency. Impedance techniques are particularly interesting, in studying mass-transport processes, roughness problems and corrosion phenomena of semiconductor electrodes in darkness and under illumination with white or monochromatic light.

In the particular case of semiconductor electrodes, complex behaviours are often associated with the occurrence of surface states in the forbidden gap. Thus the utilization of Opto-electric and Electro-optic impedance techniques becomes important. As an exemple, IR absorption response provides detailed information on the nature of the charge being displaced upon potential modulation (free carriers or surface states). The concentration of free carriers near the interface may also be probed by the surface conductivity measured at different frequencies (optical, microwave or d.c).

In all cases, interpretation of impedance spectra needs obligatory the utilization of theoretical models based on equivalent electric circuits including simple dipolar elements. Making use of resulting experimental data can be realized through different representations such as for example : Nyquist, Bode, Cole-Cole, Fourire transform (Laplace)...

Experimental data obtained by different techniques and the use of the maximum possible representations are necessary for a serious analysis in view of the detection of intermediate steps occurring in the overall process. The importance of the complementarity of these different techniques and different representations of data obtained will be elucidated in the lecture.

Modelling diffuse solar radiation using
three different approaches
M.ABDEL WAHAB^{*}, F.M.EL-HUSSAINY^{**}, A.B.MAYHOUB^{***}
AND K.S.MOHMED^{***}

ABSTRACT

Diffuse solar radiation "D" is difficultly modeled in solar energy application. Three different methods will be used to simulate this component and its variability due to scattering and absorption by particles in the atmosphere. The proposed methods were compared with the measurements, the ratio of diffuse component to direct one was found to vary with wind direction in a manner such that greater turbidity is found with southwest winds rather than other directions. It was found that the gain in "D" is associated with increased turbidity compensates for the attenuation of direct radiation by an amount that varies from 58% to 70% .

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Current Flow In CdS/Si Heterojunction Solar Cell

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Solar cell made of a p-Si crystal on which deposited thin layer of In-doped CdS has been investigated. The CdS forms an efficient optical window for the solar spectrum as it has a wider band gap and lower refractive index than silicon. The heterojunction formed of n-CdS/p-Si has been studied taking account the nonuniformities in both doping and band structure as well as the small lattice mismatch between the two materials. The study include the space charge and the interface states and its effects on the electrostatic potential. Non-equilibrium conditions have been assumed and all current components are considered. They are the tunneling current, the interface current, the diffusion current, the generation-recombination current and the photogenerated current. The study shows that none of the current components dominates, so all components are included. The maximum efficiency of the solar cell could be achieved for the thicker CdS film and larger cell area. Comparison with experimental results shows a satisfactory agreement.

Dye Photosensitized Oxygenation Of Some Quinones

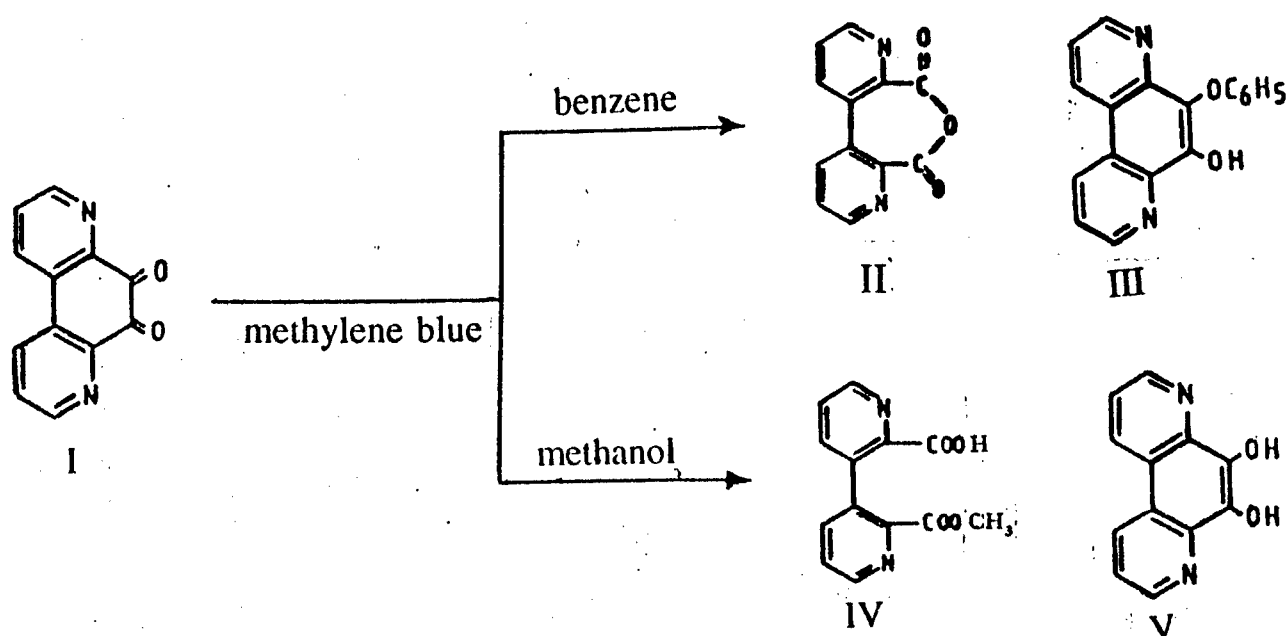
By

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The photosensitized oxygenation of 4, 7-phenanthroline-5,6-quinone (I) in presence of methylene blue resulted in the formation of products whose nature depended on the experimental conditions. In benzene, 3,3'-bipyridyl-2,2'-dicarboxylic anhydride (II) (40%) and 5-phenoxy-6-hydroxy-4, 7-phenanthroline (III) (20%) were produced. In methanol, 3,3'-bipyridyl-2,2'-dicarboxylic acid monomethyl ester (IV) (60%) and 5,6-dihydroxy-4,7-phenanthroline (V) (10%) were produced.

Structural reasoning for the compounds produced in these reactions was based on analytical and spectral data. A mechanism accounted for the formation of these compounds is given.



INDEX

KEY: 1 P A1 = PAGE 1 POSTER NUMBER A1

ABDEL-AZIM S. (EGYPT) **1 P A1**
THE RAPID DETERIORATION OF ANTHRACENE LASER DYES IN CHLORINATED ORGANIC SOLVENTS

ABD-EL-AZIZ A. S. (CANADA) **2 LEC**
PHOTOLYSIS OF POLYAROMATIC ETHERS AND THIOETHERS WITH PENDANT CYCLOPENTADIENYLIRON MOIETIES

ABDEL-LATIF F. M. (EGYPT) **3 P A2**
PHOTOCHEMICAL REACTION OF 4-NITROBENZYLIDENE MALONONITRILES WITH HYDROGEN DONORS

ABDEL-RAZIK E. A. (EGYPT) **4 P A3**
HOMOGENEOUS PHOTOINITIATED GRAFT COPOLYMERIZATION OF 4-VINYL PYRIDINE ONTO ETHYL CELLULOSE

ABDEL-SHAFI A. (ENGLAND/EGYPT) **5 P A4-5**
1- CHARGE TRANSFER INTERACTIONS AND EFFICIENCIES OF SENSITIZED SINGLET OXYGEN PRODUCTION FROM SUBSTITUTED BIPHENYLS
2- SINGLET-SINGLET ENERGY TRANSFER BETWEEN COUMARIN-4 - WATER EXCIPLEX AND COUMARINE314 IN AQUEOUS AND MICELLAR MEDIA

ABDEL-WAHAB A. A. (EGYPT) **7 P A6**
ON THE PHOTOGENERATION OF THE PYRIDYLCARBENES

ABDOU W. (EGYPT) **8 P A7**
ENVIRONMENTAL DEGRADATION OF PESTICIDES UNDER THE INFLUENCE OF LIGHT

ABO ALY M. (EGYPT) **9 P A8**
ANALYTICAL DETERMINATION OF IRON (III): FLUORESCENCE QUENCHING TECHNIQUE

ABOU-ELZAHAB M. M. (EGYPT) **10 P A9-10**
1- SYNTHESIS OF SOME POTENTIAL PHOTO-THERAPEUTIC AND SINGLET OXYGEN SENSITIZERS: HEMATOPORPHYRIN-COUMARINS (HPD-C) AND HEMATOPORPHYRIN - FUROCOUMARINS (HPD-FC)
2- PHOTOCHEMICAL REACTIONS OF DIBENZALACETONE

ABO-FARHA S. A. M. (EGYPT) **12 P A11**
THE ROLE OF INORGANIC COMPLEXES IN ENERGY CONVERSION

ABOU-ZIED K.A. (EGYPT) **13 P A12**
ENERGY TRANSFER FROM 2,5-DISTYRYL PYRAZINE (DSP) AND 2,5-BIS 2(2-NAPHTHYL) VINYL PYRAZINE (B2NVP) TO R6G

ABOU-ZIED O. (CANADA/EGYPT) **14 P A13**
STRUCTURES AND LASER INDUCED S_2-S_0 FLUORESCENCE SPECTRA OF VAN DER WAALS COMPLEXES OF AZULENE AND RELATED COMPOUNDS IN A SUPERSONIC JET

AGOSTIANO A. (ITALY) **15 P A14**
CHARGE RECOMBINATION KINETICS OF PHOTOSYNTHETIC REACTION CENTERS IN PHOSPHOLIPID ORGANIZED SYSTEMS

AHMED I. SADAT (EGYPT) **17 P A15**
THE EFFECT OF SUNLIGHT ON SOME EFFERVESCENT BEVERAGES IN THE EGYPTIAN MARKET

AL-HASSAN K. A. (JORDAN) **18 LEC**
FREE VOLUME SENSING FLUORESCENCE "TICT" PROBES FOR CYCLODEXTRINS INTERIOR

AL-JALLAL N. (KUWAIT) **19 P A16**
THE INFLUENCE OF METHOXY AND CYANO SUBSTITUENTS ON PHOTOCYCLOADDITION OF ETHENES TO NAPHTHALENES

ALI S. I. (INDIA) **20 LEC**
PHOTOEXCITATION OF TRANSITION METAL COMPLEXES IN ORGANIC SUBSTRATES

ALI S. S. (JAPAN/EGYPT) **21 LEC**
PECULIAR SPIN POLARIZATION IN THE PHOTOLYSIS OF SEVERAL Ni- AND Pt-COMPLEXES

ALONSO-VANTE N. (GERMANY) **23 LEC**
THE SIGNIFICANCE OF SURFACE STATES FOR PHOTOELECTROCATALYSIS AT THE SEMICONDUCTOR/ELECTROLYTE INTERFACES

ANTONIOUS M. S. (EGYPT) **24 P A17**
DEACTIVATION OF MULTIDIMENSIONAL S_1 -STATE OF SOME LASER DYES

AQUILANTI V. (ITALY) **25 LEC**
NONADIABATIC ENERGY TRANSFER

AZUMI T. (JAPAN) **26 LEC**
STUDIES OF PHOTOCHEMICAL REACTIONS BY NUCLEAR SPIN POLARIZATION-DETECTED ESR SPECTROSCOPY

- BABAQI A. S. (YEMEN)** **27 P A18**
A NEW DIOLEFINIC LASER DYE: 2,5-BIS-2-(2-NAPHTHYL) VINYLPIRAZINE (B2NVP)
- BADAWI A. M. (EGYPT)** **28 P A19**
TREATMENT OF WASTE WATER FROM REFINERIES BY OZONE/UV CATALYTIC PHOTOOXIDATION
- BADR Z. (EGYPT)** **29 LEC**
PHOTOLYSIS AND PYRROLYSIS OF ACID AMIDES AND SULPHONAMIDES; MECHANISTIC STUDIES
- BILLING R. (GERMANY)** **30 LEC**
SELECTIVE OXIDATION OF ALCOHOLS BY DIPHENYLIODONIUM IONS IN A PHOTOINDUCED CHAIN REACTION
- BOLTON J. (CANADA)** **31 LEC**
SOLAR DETOXIFICATION OF WASTE WATER
- BOXER STEVEN G. (USA)** **32 LEC**
MECHANISM OF THE EARLY STEPS IN PHOTOSYNTHESIS
- BRASLAVSKY S. (GERMANY)** **33 LEC**
TIME-RESOLVED PHOTOTHERMAL MEASUREMENTS ON BIOLOGICAL PHOTORECEPTORS
- CALEWELL R. A. (USA)** **34 LEC**
INTERSYSTEM CROSSING IN ORGANIC TRIPLET INTERMEDIATES
- CALZAFERRI G. (SWITZERLAND)** **35 LEC**
DYE MOLECULES IN ZEOLITES AS ARTIFICIAL ANTENNA SYSTEMS
- DMITRUK S.L. (RUSSIA)** **37 P A20**
DYNAMICS OF BARRIERLESS STRUCTURAL RELAXATION OF EXCITED PYRIDYLOXAZOLE CATIONS
- DOEPP D. (GERMANY)** **39 LEC**
REGIO- AND STEREOSELECTIVITY IN LIGHT INDUCED [4+2]-CYCLOADDITIONS OF ALPHA-CYANOENAMINES TO AROMATIC CARBONYL COMPOUNDS, NITRILES AND HYDROCARBONS
- DRUZHININ S. I. (RUSSIA)** **41 P A21-22**
1- EXCITED STATE RELAXATION PROCESSES OF CROWNED STYRYL DYES AND THEIR METAL COMPLEXES
2- TICT-STATE FORMATION DYNAMICS IN N-ALCOHOLS: N,N-DIALKYLAMINONAPHTHALIMIDES

- DUERR H. (GERMANY)** **45 LEC**
MOLECULAR AND SUPRAMOLECULAR SYSTEMS IN PHOTOCHROMISM
- EBEID E. (EGYPT)** **46 P A23**
THE EMISSION CHARACTERISTICS AND PHOTOSTABILITY OF 1,4-BIS [2-BENZOXAZOLYL) VINYL] BENZENE (BBVB) AND 1,4-BIS[BETA-(2-QUINOLYL)VINYL]BENZENE (BQVB)
- EL-KEMARY M. (EGYPT)** **47 P A24**
THE EMISSION, PHOTOSTABILITY AND COMPLEXATION ABILITY OF TETRAPHENYLPORPHYRIN (TPP)
- EL-NADI LOTFIA (EGYPT)** **48 P A25**
LASER-INDUCED DISSOCIATION OF ORGANIC IODINE GASES
- EREMENKO A. (UKRAINE)** **49 LEC**
PHOTOINDUCED ELECTRON TRANSFER BETWEEN MOLECULES IN SILICA MATRICES
- FARA V. L. (ROMANIA)** **51 LEC**
PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF DYE MOLECULES IN POLYMERS USED FOR FLUORESCENT SOLAR CONCENTRATORS.
- FASSLER D. (GERMANY)** **53 LEC**
FLUORESCENCE LIFETIMES OF ADSORBED POLYMETHINES
- FITZMAURICE D. (IRELAND)** **54 LEC**
HETROSUPRAMOLECULAR CHEMISTRY: AN APPROACH TO MODULATING FUNCTION IN MOLECULAR DEVICES.
- FUJIMURA Y. (JAPAN)** **56 LEC**
NUCLEAR WAVEPACKET STUDY OF UNIMOLECULAR REACTIONS IN ULTRASHORT PULSED LASER
- GEORGE, M.V. (INDIA)** **57 P B1**
METAL RECOGNITION AND PHOTSENSITIZING PROPERTIES OF NOVEL SQUARINE DYES
- GIARDINI A. (ITALY)** **58 LEC**
R2PI DETECTION AND SPECTROSCOPY OF VAN DER WAALS COMPLEXES OF 4-FLUOROSTYRENE WITH RARE GASES
- GRAETZEL M. (ZWITZERLAND)** **59 LEC**
NANOCRYSTALLINE SOLAR CELLS; SCIENTIFIC PRINCIPLES AND ECONOMIC PERSPECTIVES

- GREVELS F.-W. (GERMANY)** **60 LEC**
 PHOTOLYSIS OF GROUP 8 METAL CARBONYLS: TRANSIENT IR SPECTROSCOPY,
 PHOTOKINETICS AND QUANTUM YIELDS OF CO SUBSTITUTION
- GUIDO DE GUIDI (ITALY)** **62 P B2**
 MOLECULAR MECHANISM OF PHOTSENSITIZATION IN DNA
- GUILLET, J. (CANADA)** **63 LEC**
 SOLAR SYNTHESIS OF HYDROGEN PEROXIDE
- HAFIZ M. M. (EGYPT)** **64 P B3**
 CHARACTERISTICS OF Si-As-Cu SOLAR CELLS
- HARRIMAN A. (FRANCE)** **65 LEC**
 PHOTOCHEMOTHERAPY WITH CYANINE DYES
- HAU DOU-MONG (TAIWAN, CHINA)** **66 LEC**
 PHOTOCHEMOTHERAPY ON EXPERIMENTAL TUMOR WITH PHOTOFRIN II AND
 LASER
- HILL CRAIG L. (USA)** **67 LEC**
 EXCITED STATE CHARACTERISTICS AND NEW UNACTIVATED C-H BOND
 FUNCTIONALIZATION PHOTOCATALYSIS BY $W_{10}O_{32}^{4-}$
- HOFFMAN M. Z. (USA)** **68 LEC**
 ELECTROLYTE AND TEMPERATURE EFFECTS IN PHOTOINDUCED INTER-
 MOLECULAR ELECTRON-TRANSFER REACTIONS
- KADASHCHUK A. (UKRAINE)** **69 P B4**
 THE ROLE OF DOPANT DIPOLE MOMENTS ON CHARGE TRANSPORT BEHAVIOR
 IN MOLECULARLY DOPED POLYMERS
- KAMBER IVO (ZWITZERLAND)** **70 P B5**
 PHOTOCHEMISTRY AT HIGH TEMPERATURES: INTERATION OF ZnO WITH
 POSSIBLE PRODUCTS OF CO₂ REDUCTION
- KARRARAH M. A. (EGYPT)** **71 P B6-8**
 1- COMPARATIVE ELECTRON MICROSCOPY BETWEEN HYPHAE FROM YOUNG
 AND OLD CULTURES OF GAEUMANNOMYCES GRAMINIS V. TRITICI, THE TAKE-
 ALL PATHOGEN OF WHEAT
 2- EFFECT OF INFECTION WITH GAEUMANNOMYCES GRAMINIS V. TRITICI ON
 WATER ECONOMY IN WHEAT PLANT USING LEAD CHELATE METHOD
 3- FINE STRUCTURE OF THE PRIMARY ROOT OF WHEAT INFECTED WITH
 GAEUMANNOMYCES GRAMINIS V. TRITICI
- KHAN M. K. A. (BANGLADESH)** **74 LEC**
 STUDY OF A CU₂O BASED PHOTOELECTROCHEMICAL SOLAR CELLS

- KORPI-TOMMOLA J. (FINLAND)** **75 LEC**
 SELFORGANIZATION OF CHLOROPHYLLS IN HYDROCARBON SOLUTION AND IN VIVO SYSTEMS: PICO- AND FEMTOSECOND RELAXATION IN WATER BOUND CHLA AGGREGATES AND CL. TEPIDUM CHLOROSOMES.
- KOSSANYI J. (FRANCE)** **76 LEC**
 UNUSUALLY STRONG EMISSION FROM EXCIPLEXES FORMED BETWEEN BENZENOID SOLVENTS AND DIBENZOYLMETHANATBORON DIFLUORIDE
- KRISHNAN V. (INDIA)** **77 LEC**
 NON-PLANAR PORPHYRIN MOLECULAR ASSEMBLIES
- KURRECK H. (GERMANY)** **78 LEC**
 MIMICKING PRIMARY PROCESSES OF PHOTOSYNTHESIS MODEL COMPOUNDS, LIGHT-INDUCED CHARGE SEPARATION.
- LEUPOLD D. (GERMANY)** **79 LEC**
 CHARACTERIZATION OF PHOTOSYNTHETIC ANTENNAS BY NONLINEAR POLARIZATION SPECTROSCOPY (FREQUENCY DOMAIN)
- LOEHMANN SROEBEN H.G. (GERMANY)** **80 LEC**
 FLUORESCENCE OF POLYNUCLEAR AROMATIC COMPOUNDS AND MINERAL OILS IN ENVIRONMENTAL MONITORING
- LOUTFY R.O. (CANADA)** **81 LEC**
 A NON-SILVER DRY-PROCESSED PHOTOGRAPHIC ARTS FILM
- MAHMOUD A. H. H. (EGYPT)** **82 P B9**
 INTEGRATED TECHNOLOGY FOR DESERT FARMING WITH SOIL CONDITIONER "RAPG"
- MALINKA E. A. (UKRAINE)** **83 P B10**
 MECHANISM OF PHOTOCATALYTIC HYDROGEN PRODUCTION IN THE Pt/TiO_2 /OXALIC ACID SYSTEM
- MALINKA E. (UKRAINE)** **84 P B11**
 PHOTOINDUCED OXIDATION OF PYROCATECHOL OVER TITANIUM DIOXIDE
- MAZZUCATO UGO (ITALY)** **85 LEC**
 PHOTOCHROMIC MATERIALS: A COMPREHENSIVE KINETIC THERMO-DYNAMIC AND PHOTOCHEMICAL STUDY
- MEL'NIKOV M. (RUSSIA)** **86 P B12-13**
 1- PHOTORADICAL AGEING OF SOLID POLYMERS
 2- PHOTOINDUCED INTRAMOLECULAR CHARGE SEPARATION IN MIXED LIGAND DITHIOLATO- α - α' -DIIMINE ZINC COMPLEXES

- MELE A. (ITALY)** **89 P B14**
PULSED LASER ABLATION: THIN FILM PRODUCTION AND COATING, PROCESS
DIAGNOSTICS
- MOHAMED S. K. (EGYPT)** **90 P B15**
PHOTOLYSIS OF TRIAZENE-1-OXIDES
- MOLL J. (GERMANY)** **92 P B16**
THE DYNAMICS OF EXCITONS IN THE J-AGGREGATES OF A CARBOCYANINE
DYE
- MORRISON H. A. (USA)** **93 LEC**
PHOTOCHEMICAL REARRANGEMENTS OF OXAZRINDINES
- MOURAD E. A. (EGYPT)** **94 P B17**
PHOTOCHEMICAL SYNTHESIS OF TETRABRIDGED CYCLOPHAN
- NADA A. A. (EGYPT)** **95 P B18**
THE PHOTOCHEMICAL REACTION OF DIBROMO-N-METHYLMALEIMIDE WITH 1-
PHENYL-2-METHYL-1,2-DIHYDRO-3,6-PYRIDAZINEDITHIONE
- NASR CHOUHAID (CANADA)** **96 P B19-20**
1- PHOTOELECTROCHEMICAL BEHAVIOR OF COUPLED SnO_2/CdSe SEMICON
DUCTOR FILMS
2- LOW FREQUENCY CAPACITANCE MEASUREMENTS OF ALUMINUM/
MICROCRYSTALLINE CHLOROPHYLL a /SILVER SANDWICH CELLS
- NAVIO J. A. (SPAIN)** **100 LEC**
PHOTODEGRADATION OF BUTYLTIN COMPOUNDS IN WATER: ENVIRON-
MENTAL IMPLICATIONS
- OKSANEN J. A.I. (FINLAND)** **101 P B21**
FEMTOSECOND KINETICS OF CHLOROPHYLL a AGGREGATES AND
CHLOROSOMES
- OPPENLAENDER Th. (GERMANY)** **102 LEC**
NOVEL VACUUM-UV-(VUV) AND UV-EXCIMER FLOW THROUGH
PHOTORECTORS FOR WAST WATER TREATMENT AND FOR WAVELENGTHS
SELECTIVE PHOTOCHEMISTRY
- OZANAM F. (FRANCE)** **104 LEC**
IN-SITU INFRARED STUDY OF THE INTERFACIAL LAYER DURING THR ANODIC
DISSOLUTION OF A SILICON ELECTRODE IN A FLUORIDE ELECTROLYTE
- PARKANYI CYRIL (USA)** **105 P B22**

PHOTOLYSIS OF HETEROCYCLIC PESTICIDES

- RAMADAN H. (EGYPT)** **106 P B23**
NONRESONANT TRANSFER EXCITATION COLLISION OF Ca^{17+} WITH He
- RUSALOV M. V. (RUSSIA)** **107 P B24**
EXCITED STATE DEACTIVATION OF CROWDED 7-AMINOCOUMARINS
- SAUER ERIKA (GERMANY)** **109 P B25**
NON-RECIPROCITY PHOTOCHEMICAL BEHAVIOUR OF NEW 1,2-NAPHTHO-
QUINONE -(2)-DIAZO-SULFONIC ACID ESTERS
- SONG PILL-SOON (USA)** **111 LEC**
PHYTOCHROME AS LIGHT SENSOR FOR PHOTOSYNTHETIC GENE ACTIVATION
- SPANHEL Lubomir (GERMANY)** **113 LEC**
SOL-GEL SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF NANOSCALED
HYBRID MATERIALS
- TAYEB A. (EGYPT)** **114 P B25**
USE OF SOME INDUSTRIAL BY-PRODUCTS AS ENERGY STORAGE MEDIA
- TERENETSKAYA I. (UKRAINE)** **115 LEC, 116 P B26**
1- AN IN VITRO MODEL OF PREVITAMIN D PHOTOSYNTHESIS AS POSSIBLE
MONITOR OF SOLAR UVB RADIATION: KINETIC STUDIES USING TUNABLE
LASER
2- THE PROBLEM OF LIGHT SOURCE IN VITAMIN D INDUSTRIAL SYNTHESIS:
LAMP, LASER OR SUN
- TESTA A. C. (USA)** **117 LEC**
PHOTOINDUCED PROTON TRANSFER IN SUBSTITUTED PYRIDINES
- TOLBERT L. M. (USA)** **118 LEC**
EXCITED-STATE PROTON TRANSFER IN CONSTRAINED ENVIRONMENT
- UZHINOV B.M. (RUSSIA)** **119 P B27-28**
1- EXCITED STATE PROTON TRANSFER LASERS
2- RADIATIONLESS DEACTIVATION AT INTERMOLECULAR EXCITED STATE
PROTON TRANSFER OF 2,4,6-TRIARYLPYRIDINES
- WAGNER PETER J. (USA)** **122 LEC**
TRIPLET STATE RADICAL CLEAVAGE OF RING SUBSTITUENTS ON PHENYL
KETONES: DIFFERENT MODES FOR DIFFERENT ELECTRONIC STATES
- WILLIG F. (GERMANY)** **123 LEC**

INJECTION AND DISCHARGE OF PHOTO-GENERATED CHARGE CARRIERS AT
THE SEMICONDUCTOR/ELECTROLYTE INTERFACE

WULFMAN CARL (USA)

124 LEC

CATASTROPHIC POLARIZATION OF TWISTED EXCITED STATES

YANAGIDA SHOZO (JAPAN)

125 LEC

PHENAZINE-PHOTOSENSITIZED REDUCTION OF CO₂ MEDIATED BY COBALT
CYCLAM COMPLEXES

ZACHARIASSE K. (GERMANY)

126 LEC

INFLUENCE OF ENERGY GAP $\Delta E(S_1, S_2)$ AND AMINO N-INVERSION IN
INTRAMOLECULAR CHARGE TRANSFER. DUAL FLUORESCENCE AND SINGLE
CT-EMISSION

ZENKEVICH E. I. (BELARUS)

127 LEC, 128 P B29

1- DIPOLE-DIPOLE AND EXCHANGE ENERGY TRANSFER IN DIFFERENT TYPES
OF PORPHYRIN CHEMICAL DIMERS

2-ENERGY AND ELECTRON TRANSFER PROCESSES IN SELF-ORGANIZED
PORPHYRIN AND CHLORIN TRIADIC AND PENTADIC COMPLEXES

ZIMMERMAN H. E. (USA)

129 LEC

RECENT ADVANCES IN MECHANISTIC AND EXPLORATORY ORGANIC
PHOTOCHEMISTRY

LAST MINUTE ABSTRACT

ABDEL-FATTAH M. (EGYPT)

131 P A26

1-IMPROVEMENT OF HYDROGEN GENERATION BY SURFACE MODIFICATION OF
SEMICONDUCTOR ELECTRODE

2- A MODEL FOR THE CURRENT-VOLTAGE CURVE OF PHOTO-EXCITED SILICON
ELECTRODE

ABDEL-LATIF F. (EGYPT)

133 P B30

FORMATION OF 1,1-DIMETHYL 1- γ -CYANINE IODIDE FROM QUINALDINIUM
METHIODIDE UNDER SOLAR AND ULTRAVIOLET ILLUMINATION

AMER A. M. (EGYPT)

134 P A27

FLUORESCENCE PROPERTIES OF EMODINE DERIVATIVES

HAFIZ M. M. (EGYPT)

135 P A28

OPTIMIZATION OF METAL THICKNESS USED IN SCHOTTKY BARRIER SILICON
SOLAR CELL

MANSOUR A. F. (EGYPT)

136 P A29

OPTICAL STUDIES OF SOME DYES AS LUMINESCENT SOLAR COLLECTORS

SALIM A. I. (EGYPT)

137 P B31

STUDY OF THE INCOMING INFRA-RED (IR) SOLAR RADIATION AT CAIRO, EGYPT

TEGHIL R. (ITALY)

138 P A30

PULSED LASER ABLATION: THIN FILM PRODUCTION AND COATING; PROCESS DIAGNOSTICS

ETMAN M. (FRANCE)

139 LEC 33, PA31

1- STUDIES ON ANODIC DISSOLUTION OF SILICON ELECTRODES IN FLUORIDE MEDIA IN DARKNESS AND UNDER ILLUMINATION

2- INTEREST OF IMPEDANCE SPECTROSCOPY TECHNIQUES FOR CORROSION MECHANISM INVESTIGATIONS

MAYHOUB A. B. (EGYPT)

142 PA32

MODELLING DIFFUSE SOLAR RADIATION USING THREE DIFFERENT APPROACHES

HASSAN M. F. (EGYPT)

143 PA33

CURRENT FLOW IN CdS/Si HETEROJUNCTION SOLAR CELL

12/21/94 10:36 PM